THESES

belonging to the dissertation:

Microcystis aeruginosa Removal by Dissolved Air Flotation (DAF) - Options for Enhanced Process Operation and Kinetic Modelling

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1. The prospects for improved DAF process kinetic modelling rely most significantly on improving our prediction capacity of the lump particle-bubble attachment efficiency coefficient $\alpha_{pb}$. Its value largely relies on NOM (natural organic matter) concentration and composition.

2. There exists a large operational window for the improvement of the process efficiency of existing conventional drinking water treatment plants. The validity of this statement depends, however, on local circumstances and should be subject to pilot plant and cost-benefit analysis.

3. Cyanobacteria being the perfect environmental opportunists, their behaviour is pandanus to similar human manifestations of an ethically impoverished, overly competitive and unscrupulous society.

4. With the development of membrane technology, particle characterisation methods will become even more important than they currently are for conventional water treatment.

5. The dose of cynicism that any human being can take without harmful side effects on his physical and psychological health is directly proportional to the quantity of humour that accompanies it.
6. Drinking water treatment research until the fifties was mostly an art based on practical experience, evolving until the eighties into extensive attempts to mathematical model the various treatment processes' kinetics. The nineties have brought a more synergistic research approach which combines piloting, kinetic modelling and qualitative description of occurring phenomena; this emerged from the acquired notion that comprehensive deterministic representation of the large number of process phenomena is too complex and/or does not add to accuracy.

7. The road to heaven is probably more exciting than heaven itself; I do not dare comment on hell.
MICROCYSTIS AERUGINOSA REMOVAL BY DISSOLVED AIR FLOTATION (DAF)
Microcystis aeruginosa Removal by Dissolved Air Flotation (DAF)

Options for Enhanced Process Operation and Kinetic Modelling

DISSERTATION
Submitted in fulfilment of the requirements of the Board for the Doctorates 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, 26 January 1998 at 13:30 h

by
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Abstract


Seven Dutch surface water treatment companies share the problem of periodical troublesome algal blooms in their raw water sources and reservoirs, and participated in this research: Amsterdam Water Supply (GWA), North Holland Water Supply Companies (PWN), Rhine-Kennemerland Water Transport Company (WRK), Dune Water Supply Company South Holland (DZH), Energy and Water Supply Company Rhineland (EWR), Water Supply Association Overijssel - Regio Oost (WMO, formerly Water Supply Company Oost-Twente - WOT), and Groningen Water Supply Company (GWG). KIWA Research and Consultancy also participated actively in the research.

The eutrophication status of the raw water utilised by the water treatment companies varies substantially. Phosphorus was found to be the limiting nutrient; concentrations of >0.05 mg P/L were recognised as potentially troublesome in terms of algal growth (>10 μg chlorophyll-a/L). The predominant algal species depend on a range of additional factors, including pH, temperature, combined ratio of other nutrients, light availability, etc. Different sets of problems are experienced due to the resultant seasonal algal population fluctuations (from 8.4 μg/L chlorophyll-a for Loenderveen Lake to 238 μg/L chlorophyll-a for the PWN reservoir, on a yearly average maximum basis). In all cases however, the periodical peak concentrations of algae cause substantial treatment problems. Cyanobacteria in general and the Microcystis aeruginosa and the Oscillatoria agardhii species in particular, proved to be the most persistent and associated with most treatment problems. The Dutch experiences are generally representative of industrialised countries where increased eutrophication results commonly in algal blooms and related treatment problems. These included an up to 100% higher coagulant dose, substantially increased filter backwash quantities, trihalomethane formation (during short periods of intermittent chlorination for mussels growth control), (surface) clogging of filters, passing of algae through treatment in objectionable quantities, increase of MFI (modified fouling index) and AOC (assimilable organic carbon) values, etc. The spherical M. aeruginosa single cells form is also representative of particles in the size range that are typically difficult to remove in treatment (3-10 μm). Its size and shape make it also a suitable representative of the pathogenic Cryptosporidium oocysts and Giardia cysts.

This study targeted the removal of the cyanobacteria M. aeruginosa by conventional and advanced treatment technologies, that are available or considered feasible under raw water quality and process circumstances that are typical for the Netherlands. The ultimate barrier preventing them, and their products, from penetrating into the distribution system is rapid or/and slow sand filtration. Pre-treatment modes practised in the involved companies include sedimentation-
filtration and more advanced dissolved air flotation (DAF)-filtration. The coagulation/flocculation process is of critical importance regardless of the down-stream treatment; however, the down-stream treatment itself is defined by the coagulation/flocculation. The option of algae conditioning by oxidants, e.g. ozone or KMnO₄, although not actively practised in the Netherlands, was considered attractive to (periodically or continuously) increase the algae removal efficiency. Consequently, this study aimed to investigate a range of treatment options for the removal of *M. aeruginosa*, with an emphasis on DAF and different modes for its enhancement. The evaluation of process efficiency was to be complemented with insight into the process mechanisms, and to serve as a basis for the evaluation of process kinetics.

For this purpose two experimental modes were used: a bench-scale modified jar test filtration apparatus with facilities for both DAF and sedimentation, and a commercial DAF pilot plant (Purac, Sweden). The former utilised model water prepared by spiking water originating from the Biesbosch reservoirs (the Netherlands) with laboratory cultured *M. aeruginosa* to a standard initial concentration of ≈ 10,000 cells/mL. The standard experimental temperature was 20°C and coagulation G was 1,000 s⁻¹ for 30 s at pH 8. Other coagulation pH conditions were also tested (pH 4, 6, 7, 8, and 9). The flocculation G and time were varied (G=10, 30, 50, 70, 100 and 120 s⁻¹ and t=5, 10, 15, 25, 30 and 35 min). The coagulant (FeCl₃ · 6 H₂O) doses were 0 - 15 mg Fe(III)/l, while the cationic polyelectrolytes Superfloc C-573 and Wisprofloc-P, the non ionic Wisprofloc-N, and the anionic Superfloc A-100 were tested as sole coagulants and as coagulant aids. Ozone was used as an algae conditioner in the dose range of 0.48-2.16 mg O₃/L, or 0.2-0.9 mg O₃/mg TOC at pH 7.5. KMnO₄ conditioning was tested in the dose range of 0-2 mg/L at pH 8, the optimal dose being based on the visual determination technique. The KMnO₄ contact time was varied from 0-30 min. The DAF pilot plant was (operated at a flow of Q=4-6 m³/h) followed by a multi media rapid sand up-flow filtration (Q=0.4 m³/h, v=10 m/h) and situated at the WRK III treatment plant in Andijk, the Netherlands. It was compared with the full-scale WRK III treatment line comprising of flocculation, lamella sedimentation and filtration, during the cyanobacteria blooms (primarily *M. aeruginosa*) occurring in the raw water reservoir. Analytical techniques for the assessment of process efficiency included turbidity, residual coagulant (Fe), TOC/DOC, UV absorbance at 254 nm, and residual Mn. They were supported by more advanced methodologies including bromate and MFI measurements, particle count (in the size range of d>2.75 μm and in a limited number of cases d>0.3 μm) and computer image analysis (d>1.9 μm). Coupled with the high resolution SEM (scanning electron microscopy), the latter provided valuable information for assessment of process mechanisms and kinetics.

DAF proved to be a viable and efficient alternative to sedimentation for the treatment of heavily algae (*M. aeruginosa*) laden water. It consistently resulted in equal or better algae removal efficiency than the sedimentation process (71% versus 87% for jar test conditions, and 96.3% versus 95.9% for pilot plant conditions), requiring at the same time an up to 50% lower coagulant dose than the sedimentation (3 mg Fe(III)/L versus 10 mg Fe(III)/L in the jar test conditions, and 7-12 g Fe(III)/m³ versus 20-24 g Fe(III)/m³ + 0.2-0.5 g Wisprofloc-P/m³ in the pilot plant conditions and the full scale sedimentation), which is significant from an environmental point of view. Also, the produced sludge was of high solids content. Other positive aspects included the relatively short flocculation time (however, not shorter than 15 min, compared to >30 min for sedimentation) and the low flocculation energy input requirement (G=10 s⁻¹ compared to G=30 s⁻¹ for sedimentation), as well as the high process loading rate (leading to 5-6 times overall lower space requirements). Furthermore, the DAF-filtration treatment scheme resulted consistently in
high (>2 log) algae removal efficiency. The relatively low coagulant demand for DAF, however, produced less efficient sweep coagulation conditions than in the case of the sedimentation, resulting in organo-Fe complexes formation and consequently higher DAF effluent Fe and turbidity residuals. This was overcome by coagulation at pH<IEP (iso-electrical point), suggesting the potential of using cationic polyelectrolyte coagulant aids. These improved the particle (algae) removal efficiency significantly in case of the model water experiments (20-40%), compared to a minor rise of only 1-2% in pilot plant experiments. This is owed to the promotion of particle (algae) adsorption coagulation based on charge neutralisation. Furthermore, the observed charge neutralisation phenomena resulted in improved particle-bubble attachment and hence more efficient DAF. Non-ionic and anionic polyelectrolytes (and the bridging mechanism) were found to be less efficient, partly because of the lower particle concentration (lower coagulant dose) and the negative charge of the air bubbles.

The particle (algae) removal efficiency the pilot plant achieved on reservoir water was by 20-30% higher than that in the jar tests with model water. The NOM (natural organic matter) concentration and composition was found to be the likely cause of the differences, especially as it is present in the form of organic matter meshes and fibrilar structures. Although the complexing of metal coagulants by NOM imparts additional coagulant demand, these structures may eventually promote flocculation, serving as sites for easier floc growth and embedment, as well as providing a gel-like structure that is easier to be removed by the rising air bubbles in DAF.

Relatively low doses of ozone (0.2-0.5 mg O₃/mg TOC, or 0.6-1.5 mg O₃ /L) as an algae conditioner under bench-scale conditions significantly (by 30-40%) increased DAF efficiency towards 2 log removal. Combined with cationic polyelectrolytes, the DAF process efficiency rose further typically by another 5%. Although not yet confirmed by pilot plant results with reservoir water, the application of the lower dose range of 0.2 mg O₃ /mg C at pH 7 resulted in bromate levels within the range of the 10 μg/L MAC prescribed by the EU. The further improvement of organic matter removal by down-stream GAC (granular activated carbon) filtration would enhance interest in this treatment, especially if ozone is already used for other purposes within the plant (e.g. disinfection), and providing the MAC value remains within the currently prescribed range.

The use of KMnO₄ as an algae conditioner also tended to increase DAF process efficiency towards 2 log particle removal, resulting in equal or better performance than the full-scale conventional sedimentation, on occasions even better than the full-scale sedimentation + filtration in terms of particle (dₚ>2.75 μm) removal. However, the resultant higher effluent Fe (organo-Fe complexes) and Mn (mostly MnO₂) concentration raised the particle count in the colloidal size range (<0.5 μm) and the turbidity. This situation improved when cationic polymers were introduced as coagulant aids, significantly improving the DAF process efficiency (typically by 5%) on the account of reduced Fe and Mn residuals below their respective MAC values. This option, however, did not lower the accompanying filtrate MFI value to the desired 5 s/L² value. The lowest MFI value achieved by the non-optimised filtration (within the DAF + filtration scheme) was in the range of 20 s/L². This suggests the need for optimisation of the filtration step to fully utilise the conditioning benefits of KMnO₄.

The improved algae removal in the case of conditioning by an oxidant is probably caused by a number of process mechanisms. Motile algal cells are immobilised by the oxidation of the outer
cell layer, and their metabolic processes are disrupted. This is accompanied with the creation of stress conditions in the algal environment, resulting in EOM (extra-cellular organic matter) excretion, partial algae lysis and IOM (intra-cellular organic matter) leakage. The EOM and IOM act as natural coagulant aids, resulting in spontaneous microfloculation even before coagulant addition. Oxidation and removal of the organic coating on the particles, as well as oxidation of NOM, result in more favourable coagulation conditions through the production of in-situ coagulant, which otherwise would have been complexed and unavailable for coagulation. The resultant MnO₂ in the case of KMnO₄ conditioning increases the particle concentration and promotes sweep coagulation.

The particle size frequency and volume distributions obtained under different process conditions and after different process stages served as the basis for an empirical calculation of the relative and absolute floc density, an input variable in the single collector collision efficiency DAF reaction zone model. Other input variables such as the mean particle (floc) and bubble size, as well as their number and volume concentrations, were also directly measured or calculated. The calculated values for the particle-bubble attachment efficiency αₚₐ support the previous assertion regarding the positive impact of cationic polyelectrolytes, and conditioners. Results suggest that under optimal DAF process conditions almost every second particle (floc)-bubble collision resulted in their attachment. The role of the recirculation ratio (5-10%) and the saturator pressure (500-700 kPa), although significantly affecting the bubble size distribution, proved less important for DAF process efficiency. Thus, critical attention should be paid to the coagulation/floculation process as the major determinant of DAF efficiency. Although difficult to model, the impact of NOM concentration and characteristics on the particle-bubble attachment efficiency is of great significance. Thus, the simplified modelling approach that particle-bubble agglomeration is solely the result of their collision is not fully justified.

DAF proved to be an efficient, robust and flexible water treatment process, and a highly appropriate alternative to sedimentation for the treatment of algae laden water. The lower civil engineering costs and chemicals consumption often will compensate for the higher energy and maintenance costs. Its high algae removal efficiency makes it particularly attractive as pretreatment before direct filtration, or membrane filtration. Where it is already applied, it's efficiency can be significantly enhanced temporarily (e.g. during short or long term algae blooms) by the application of e.g. cationic polyelectrolytes, oxidants, or a combination of the two. The application of KMnO₄ seems particularly attractive, since no hazardous by-products are produced. Similarly existing sedimentation units can be retrofitted with (enhanced) DAF in case of increased algae problems. Nevertheless, the final choice of the treatment technology or mode should be made after pilot plant investigations and cost-benefit analysis.
Chapter 1

THE ALGAE PROBLEM IN THE NETHERLANDS FROM A WATER TREATMENT PERSPECTIVE

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ABSTRACT: Surface water treatment in the Netherlands receives increased attention requiring better characterisation and evaluation of the 'algae problem'. Investigations and analysis carried out at five drinking water production locations in the Netherlands utilising surface water (amounting to 60% of the overall Dutch surface water production) show that the most significant problem are the cyanobacteria. Seasonal blooms of Microcystis aeruginosa and Oscillatoria agardhii force short- and long-term process modifications, affecting water production cost. Assessment of possible solutions suggests that, apart from the application of appropriate water quality management measures, new insights on more efficient (pre)treatment processes are critical. In treatment, the agglomeration (coagulation/flocculation) phase is considered the essential step in the removal of the algae. It should be optimised in relation to the pre-treatment preceding it (e.g. application of chemical oxidant/s, and/or microstraining), as well as to the applied solid-liquid separation treatment process. Dissolved air flotation (DAF) emerges as a feasible option given the natural tendency of algae to float. The existing discrepancies between literature and practice call for further research on process mechanisms and suggest that considerable gains can still be made in process optimisation. This research should notably increase insight into the influence of algae morphology and physiology on treatment efficiency.

1.1 INTRODUCTION

1.1.1 Algae in water supply - a growing concern

VEWIN (the Association of Dutch Water Supply Companies) forecasts the drinking water production in the Netherlands to amount to 1360 Mm³/year by the year 2000, of which 16% (220 Mm³/year) will originate from treated surface water, another 16% (220 Mm³/year) from dune-infiltrated water, and the remainder (930 Mm³/year) from groundwater [1]. Although this projection for all the sources shows a substantial amount of the infiltrated water is of surface water origin, surface water is not recognized by VEWIN as the preferred alternative. Very often it contradicts one or more of the four basic principles that have to be met for any water source: (i) good water quality, (ii) constant water quality, (iii) low treatment cost and (iv) security from calamities. Nevertheless, surface water is an inevitable choice due to increased water consumption and increasing number of restrictions on groundwater abstraction. The main surface water sources in the Netherlands are the rivers Rhine and Meuse. These two rivers receive a substantial industrial, municipal and agricultural pollution load, resulting in water treatment problems such as high turbidity, colour, organic micropollutants content and high nutrient loads. Eutrophication is recognized as the cause of numerous problems, both in surface water quality and in drinking water treatment. It causes plankton blooms in stagnant and slowly flowing water bodies; their removal emerges as a priority problem in surface water treatment.

Algae cause a wide range of technical and health problems in the treatment and in the distribution step [2]:

i) problems related to algae laden water treatment:

- interference with coagulation and flocculation;
- increased disinfectant demand of the water;
- production of haloform precursors;
- filter clogging and increased use of backwash water; and
- filter penetration;

ii) problems related to algae presence in the distribution system:

- taste and odour;
- precipitation of algal mucopolysacharides at low pH;
- corrosion of iron mains and discolouration of water;
- shielding of pathogenic bacteria from disinfection;
- aftergrowth of bacteria and higher organisms in the mains;
- infestation of zooplankton; and
- release of toxins.

Nevertheless, water supply experts disagree about the required degree and approach to algae removal in water treatment. Lacking a proper water quality standard, one has to rely on the philosophy that the more algae are removed during common treatment, the better, accepting however that removal efficiency for different types of algae varies widely. The diversity of algal species with respect to their size, form, surface characteristics, production of extra-cellular organic matter (EOM), motility, etc., makes it almost impossible to propose a simple solution that fits water quality management and treatment concerns. Therefore, the 'best available technology' for treatment tends to set the standards.

This chapter intends to address the issue of raw water quality for five Dutch surface water resources, contributing to approximately 60% of the total surface water origin treated water in the Netherlands. Statistical analysis of the water quality parameters contributing to the eutrophication phenomenon will be performed. This will be related to the resultant impact on the algal population, quantity- and species-wise, defining the most significant species from the point of view of imparted treatment problems. The treatment problems, as well as the adopted short and long term reservoir management and treatment strategies will also be discussed. Finally, an overview of existing conventional treatment technologies, as well as more advanced options for their enhanced operation, will be discussed in the context of most efficient algae removal in drinking water treatment.

1.1.2 Eutrophication and algae

Long term changes in the nutrient supply to water bodies cause shifts in the balance and spectra of resources to which phytoplankton is known to respond quantity- and quality-wise. Such changes occur naturally due to a variety of causes. The large increases in the amount of nutrients discharged into water bodies during the past decades, especially in the industrialized countries, and the subsequent changes in the ecology of these water bodies, have called attention to the problem of nutrient enrichment, or eutrophication. Generally, the adjective 'eutrophic' (="well feeding") is used to describe biological aquatic systems with a high input of otherwise growth limiting nutrients, and which therefore support a high level of organic productivity [3].

Eutrophic conditions occur naturally (by leaching of soils and vegetation decomposition), but are nowadays primarily due to human activities (domestic sewage, agricultural run-off, etc.) [4]. The anthropogenic eutrophication, should be tackled at the source of the nutrients discharge, rather
than by the symptoms. In the Netherlands, as well as in some other West European countries, measures like tertiary sewage treatment and a ban on detergent phosphate have drastically reduced nutrient inputs. However, the nutrient rich under-water sediments, the contained fertilizer use in agriculture, and the inevitable leaching of N and P from wastewater, will keep the trophic levels high.

Eutrophication manifests itself as increased water fertility which results in higher primary productivity, i.e. algal growth. Under extreme conditions this can lead to temporary excessive algal biomass and ecosystem instability. As a result of increased eutrophication, the diversity of algae, especially with respect to the planktonic forms, is reduced in favour of large concentrations of a limited taxonomic range of cyanobacteria, chlorophytes and diatoms. The trophic level of the water body thus defines the range and concentration of species present within it [3].

A common annual cycle for eutrophic impounded water in northern temperate regions like the Netherlands consists of a spring population of diatoms which may include *Asterionella formosa*, *Fragilaria crotonensis*, *Tabellaria flocculosa*, *Melosira* spp., *Cyclotella* spp., *Stephanodiscus astraea*, and/or *S. hantzschii*. During early summer, diatoms may be replaced by small species of cryptophycea or chlorophycea, and at a later stage by dinoflagellates such as *Ceratium hirundinella*, chrysophytes such as *Dinobryon* spp., *Synura* spp., or chlorophyte genera such as species of *Chlorella*, *Scenedesmus*, *Dictyospherium*, *Ankistrodesmus*, *Eudorina* and *Pandorina*. However, in late summer and throughout autumn, dominant populations of cyanobacteria (blue-green algae) may occur, including *Anabaena* spp., *Aphanizomenon flos-aquae*, *Gloeotrichia*, and *Coelosphaerium*, especially *Microcystis aeruginosa* and *Oscillatoria* spp. can be abundant and are able to form surface blooms of aggregated cells under windless conditions [4].

In addition, cyanobacteria tend to dominate a large part of the growing season. Objectionable odours may emanate from water bodies due to decaying biomass, and the water may suffer from offensive tastes and odours, while serious disruption of water treatment processes is experienced. Predation of algae is reduced by colony forming and filamentous cyanobacteria, resulting in the preclusion of effective filter feeding zooplankton (algae size related). This further influences the plankton abundance and composition. In addition, toxins produced by cyanobacteria, such as microcystin, have been responsible for occasional outbreaks of wildlife and livestock illness and death, and has been related to human illnesses [4].

Principles of freshwater ecology phytoplankton form the basis for appropriate design and management strategies of lakes and reservoirs [3]. On the other hand, knowledge of the freshwater ecology does not guarantee the accurate prediction of the plankton responses to particular changes in their environment. Furthermore, the primary problem of water treatment engineers in practice is the problem of biomass 'peaks', composed of different dominant species, regardless of the average level of biomass. Therefore, more knowledge is needed on the behaviour and characteristics of individual organisms. This knowledge should preferably overcome the indiscriminative algae related lumped material parameters approach (chlorophyll, organic carbon, turbidity, etc.). Species differ in their ecological, morphological and physiological characteristics that allow them to survive and grow, and that can strongly influence water treatment.
1.1.3 Growth strategies and characteristics of cyanobacteria

The spatial and temporal distributions of an organism within an ecological system are the result of the evolutionary strategies the organism adopted for growth and survival [5]. Strategies can be defined as sets of similar morphological, physiological, reproductive or behavioural traits that have evolved among species or populations and that are better suited to particular environmental conditions than that of others. Accordingly, different organisms that adopted similar strategies, are likely to resemble in their ecological behaviour.

Based on the logistic growth equation phytoplankton communities have commonly been classified into two main categories: r (characterised by rapid growth and colonisation of a nutrient rich environment) and K (characterised by the ability to out compete other organisms in a nutrient limited environment) [3]. However, other approaches exist that are seemingly more suitable for algae and which classify organisms into three categories marked C, S or R [5]:

- C/competitors: exploitation of environments saturated with light and nutrients, through the investment in rapid growth and reproduction, and to do so before other species;
- S/stress tolerant: operation under conditions of severe depletion of externally supplied essential nutrients; and
- R/ruderals: tolerate frequent or continuous turbulent transport through the light gradient.

There is a considerable overlap of morphometric and physiological characteristics (e.g. unit volume, surface area/volume, maximum linear dimension, photosynthetic efficiency, projected area, maximum growth rate, cellular phosphorus uptake, temperature sensitivity, threshold dose of exposure to saturating light intensity, motility, minimum sinking rate and susceptibility to grazing) of these classes, but the growth and recruitment of a particular strategist will be preferentially promoted in function of specific environmental circumstances. These species are then more likely to build up the largest fraction of sustainable biomass (i.e. become dominant) for as long as the same circumstances persist.

Environmental variables that are supposed to influence the selection among the primary strategists (C, S or R) may be grouped as physical factors (e.g. temperature, stability of the water column, absolute mixed depth, turbidity of mixed layer), chemical factors (notably nutrient concentration) and biotic factors (grazers filtering rate). These may be referred to as externally imposed (allogetic) perturbations. On the other hand, self-imposed (autogenetic) perturbations play a substantial role in the definition and selection among the strategists, like euphotic depth (depth of light penetration), reduction due to high biomass concentration, nutrients concentration decline, or increased rate of zooplankton grazing.

Extreme eutrophication expressed in a range of unusual physio-chemical conditions has been proven advantageous to the physiologically and ecologically adaptive cyanobacteria. Ideally, physical and to a lesser extent chemical stability must accompany such extremes. The more a species is versatile in adapting itself to a wider set of survival associated factors, the more abundant, and the longer lasting is its population during the yearly cycle [5]. The cyanobacteria have proven to be highly versatile and adaptable, able to survive and to dominate in conditions highly unfavourable for other species. This versatility makes cyanobacteria able to survive and dominate in water bodies during protracted periods of the annual plankton cycle. In some
relatively large and shallow lakes, e.g. the Hartbeespoort Dam and the Vaalkop Dam in South Africa, cyanobacteria compose the most significant part of the population throughout the year; this situation probably reflects a final eutrophication stage of a lake, considering the comparatively constant climatic and nutrient conditions [6].

Carbon, nitrogen and phosphorus are the essential nutrients for cyanobacteria. The nutrient uptake pattern influences the population structure in the water body. It has been noticed that high phosphorus levels generally result in cyanobacterial dominance, though blooms also occurred in low or undetectable phosphate concentrations [7]. The latter is probably caused by fast and almost complete uptake of phosphate by blooming species, leaving the water with low phosphate concentrations for a period of time. A large diversity in response towards phosphorus deficiency has been found, with little or no growth rate dependence on external (i.e. soluble reactive phosphorus, or total dissolved) phosphorus. The rate of phosphate uptake is optimal between pH 7.5 and 8.5 and declines sharply below neutral pH; it is larger in light than in dark conditions.

Most cyanobacteria are N₂ fixing organisms [7]. Fixation of dissolved atmospheric N₂ fixation is carried out by unicellular organisms, by filamentous, heterocystic forms (such as Anabaena and Nostoc) and by filamentous strains lacking heterocysts (heterocysts and akinetes emerge in nutrient exhausted surroundings, akinetes having a preservatory role and being able to germinate in better nutrient conditions).

The role of carbon in the nutrition and life cycle of cyanobacteria is still not sufficiently clarified, but together with nitrogen it is readily available from the atmosphere, unlike phosphorus. The deficiency in nitrogen and phosphorus is known to lower the respiration rate, and causes accumulation of carbohydrates during the light period of the day, preparing cells for survival in the dark [7].

Cyanobacteria depend on efficient photosynthesis. Like other taxa, they show phototactic/phobic and chemotactic/phobic responses, indicating their affinity to light and limnological conditions. Cyanobacteria, however, are versatile and adaptive, which allows them to out compete other algae in unfavourable environments with regard to nutrients and light. They can adapt to the light-dark regime in a way that gives them the possibility to maintain a higher photosynthetic activity during short photoperiods, so that they may survive for prolonged periods in the dark. They can also adapt to irradiance intensity, whereas a planktonic species from a temperate lake may be killed by prolonged exposure to irradiance exceeding a certain high intensity. A characteristic adaptive mechanism adjusts their chlorophyll content to the light’s wave length, to maximize light-efficiency [7].

Cyanobacteria also show motility within the water column. Two types of movement are exerted by cyanobacteria when searching favourable living conditions [7]: phototactic gliding of cyanobacteria attached to surfaces (of suspended sand, clay particles, etc.), and light regulated buoyancy. The rate of displacement, and the frequency of path reversals are related to e.g. the vertical movement in a water body, and are influenced by temperature, viscosity and chemical factors. On the other hand, factors that change rapidly or a concentration gradient, like light intensity, wind and chemical factors, influence the direction of the movement.
Finally, circumstantial evidence exists that some cyanobacteria secrete organic substances of which some are inhibitory or toxic to other organisms, including fish, waterfowl, domestic livestock, and humans [3]. An assessment from almost 300 sites all over the world, in the period 1981-1989, shows that the likelihood of an individual bloom being toxic is 45-75%. Usually, *Microcystis*, *Anabaena*, *Oscillatoria* and *Aphanizomenon*, and less often *Gomphosphaeria*, *Coelosphaerium*, *Nodularia*, *Nostoc* and *Cylindrospermum*, were involved [8]. Research conducted on toxic algae blooms in the UK in 1989 indicated associated death of dogs and sheep, and illness in people. The toxicity was attributed to microcystin poisoning, originating from *M. aeruginosa*. Such blooms and associated toxicity were also recorded in Norway, Denmark, Sweden, USSR, Finland [8], Australia [9] and Brazil [10]. In Finland, cattle poisoning attributed to cyanobacterial blooms took place at three sites in 1985 and 1986, and similar blooms occurred in drinking water sources as well. The isolation of strains of cyanobacteria confirmed the presence of hepatotoxic and neurotoxic strains of *Anabaena*, as well as hepatotoxic strains of *Microcystis* and *Oscillatoria* [11]. The National Rivers Authority in UK reported in 1990 about the 1989 cattle kill and human infestations. 68% of the 78 water bodies tested for toxicity were found positive, which was related mostly to the presence of *M. aeruginosa*, though other cyanobacteria were present as well, notably *Aphanizomenon flos-aquae*, *Anabaena*, and *Oscillatoria* [6]. In 1990 the incidence of *Anabaena* spp. bloom in a recreational lake in the Netherlands was found to have caused summer flu in humans. Toxicity analysis of water containing *Microcystis* spp. blooms and originating from the Andels Meuse and Braassem Lake in the Netherlands showed the presence of hepatotoxic microcystin toxin, This led to the conclusion that consumption of these toxins via drinking water is possible [12]. Further research was advocated on the influence of environmental factors on the characteristics and levels of cyanobacterial toxicity, as well as on the stability and persistence of the toxins involved.

No consensus exist in literature on the question whether cyanobacterial toxins are relevant from the point of view of water treatment and distribution. However, it is suggested that the public health aspect should receive more attention. Distinction is to be made between physical contact with surface water containing cyanobacterial toxins, consumption of such water, and consumption of water that contained cyanobacteria before treatment. Similarly, it still is uncertain whether the toxic substances, rarely identified, are secreted by viable algae, or whether they are produced during putrescence of algal matter [3]. Significant levels of toxins found during water treatment may be provoked by cell lysis due to for example oxidants application.

Controversy also exists regarding the nature of the human infestations caused by ingestion of cyanobacterial toxins. Some species of cyanobacteria have been identified as causing gastroenteritis, however, only when consumed in large numbers [13]. High cyanobacteria concentrations in the raw water supply have been found to cause an epidemic of pyrogenic reaction among kidney patients consuming such water [14]. Lysis of cyanobacteria, when an algicide or oxidant disinfectant is applied, may result in harmful concentrations of toxins in domestic water supplies causing liver injury, gastroenteritis, or hepatoenteritis [15]. Others on the other hand, state that conclusive evidence exists that cyanobacterial toxins are a health hazard in drinking water [4].

However, not all cyanobacteria species are toxic, and differences exist between strains of the same species. The recognition of different environmental conditions (nutrient composition, light availability, presence of competitor algae species, etc.) and the governing mechanisms which may
result in differing toxicity of the same strain at different locations, has not been addressed so far and deserves further research attention.

In conclusion, it appears that the excretion of toxins is a widely recognized problem, and that high cyanobacteria concentrations warrant much caution. It is therefore recommended that a careful approach is adopted to the application of certain chemicals such as oxidants (e.g. ozone or KMnO₄) as particle (algae) conditioners due to the potential danger of toxins leakage from ruptured algae cells. The fate of toxins along the treatment line, especially the final product toxin levels deserves research attention. The issue of long term toxins consumption and health implications has not been addressed so far and also attracts attention. The recommended approach is to face and assess the potential toxicological problems regardless of the high cost and long duration of such analysis.

1.1.4 Microcystis and Oscillatoria spp.

Whilst cyanobacteria species are generally recognized as K-strategists, species differ with regard to their R or S character. The most widely spread cyanobacteria are Microcystis spp., which are characteristic for eutrophied lakes, and a typical S-species, able to dominate periods of late summer (high temperatures), and severe nutrient depletion. Their physiological and morphological characteristics make them a particular nuisance in water treatment. On the other hand, in the Netherlands concern grows about the incidence of the Oscillatoria spp. in some water resources. Oscillatoria spp. are known to possess an effective light-capturing mechanism across a wide band of the visible spectrum, as well as a buoyancy regulating mechanism. These make for a pronounced R-species, allowing the species to inhabit constantly mixed lake environments [5]. There is obvious differentiation between these two cyanobacterial genera, with respect to their shape, size, extra cellular organic matter (EOM) characteristics, nutrient uptake, buoyancy regulating mechanism, etc. On the other hand, they are both identified as cause of numerous problems in water treatment [4, 6, 8, 12, 16, 17, 18]. Therefore, they are of particular further interest to this study.

Microcystis spp. are encountered worldwide. They are spherical in shape, of 3-7 μm in size, and can occur in irregularly shaped colonies of often more thousands cells, as well as single cells. There are indications that the single cell form is an adaptation of this species developing at later stages of their life cycle (i.e. later during the season), due to the dissociation of colonies in order to provide better light availability for all cells. These species favour warmer water (>14 °C) and stable, relatively low nutrient availability, combined with stable hydraulic conditions [3, 16].

Oscillatoria spp. are characterized by an oscillating movement and lack of definite sheath. Their cells exceed 100 μm in length and are 3-5 μm in diameter; trichomes are solitary or intermingled, forming non-parallel bundle-like structures. Generally, they inhabit temperate lakes of two distinct types: (i) mildly eutrophied, large, deep, and usually alpine lakes, and (ii) shallow, enriched, unstratified basins, where they form stable maximum concentrations in the summer metalimnion, provided that this is located within the euphotic zone. They possess an extremely efficient light capturing mechanism, functional across a wide band of the visible spectrum, favouring low irradiance and achieving maximum growth rates at relatively low nutrient availability [3].
Cyanobacteria in general, and especially *Microcystis* spp., are also able to survive in conditions unfavourable for other species. For example, *Microcystis* spp. can overcome O₂ toxicity. With the high light irradiance of late summer, and high O₂ concentrations and low CO₂ concentrations, O₂⁻ (superoxide) is produced that damages cytochromes, pigments and other segments of the algal photosynthetic system. To prevent the toxicity of O₂⁻ the enzyme superoxide dimutase (SOD) is manufactured in algal cells. However, prolonged high light intensity triggers a drop in SOD level and die-off of algae. This phenomenon has been observed with most algal species, except for *Microcystis* spp. which are able to maintain high levels of SOD and survive such conditions [7].

Characteristic for *Microcystis* spp. and *Oscillatoria* spp. is the existence of gas vacuoles [7]. Up to 10,000 of these organelles are present in a single cell. Generally they have the shape of a hollow cylinder of 70 nm diameter with a conical cap at each end. They are composed of protein, the wall being permeable to dissolved gases in surrounding liquid, but unpermeable to liquid (the pressure inside being usually atmospheric). Nutrients as well as Cl⁻ and K⁺ uptake are known to play a major role in rise or fall of turgor (difference in hydrostatic pressure between the inside and outside of the cell) and consequent buoyancy. This enables the cells to attain an as good as possible position in a water body (mostly in the vertical sense) with regard to light and nutrients [7].

Other characteristics of the genera establishing their dominance are: allelopathy and light attenuation [7]. Allelopathy involves chemical inhibition of other organisms by the excretion of inhibitory organic compounds. Attenuation of light occurs as the cyanobacteria can increase their biomass very fast, thus increasing turbidity and limiting the growth of competitors. Cyanobacteria are vertically motile during diurnal or higher order nutrient fluctuations, favouring them as inhabitants of water bodies during the late summer and autumn. In addition *Oscillatoria* spp. are able to maintain approximately neutral buoyancy, and cannot be ingested by grazing zooplankton because of their length of >100 μm, ensuring low loss rates [3].

However, characteristic differences exist between the two genera with respect to nutrient affinity and uptake. *Oscillatoria* spp. have been reported to fix nitrogen [3]. *Microcystis* spp. in contrast, have been reported as non-nitrogen-fixing species [7]. Low N/P ratios can be expected to favour N₂ fixing *Oscillatoria* spp., whilst the opposite would favour the growth of *Microcystis* spp.

The toxins related to cyanobacteria blooms may be grouped into three families: neurotoxins, lipopolysacharide endotoxins, and hepatotoxic peptides. Microcystin belongs to the hepatotoxic family and is a potent and specific in vitro inhibitor of phosphatases, with an action similar to that of the tumour promoting toxin of shellfish poisoning, okadaic acid. This particular toxin, consists of polypeptide containing D-serine, L-ornithine and some protein L-amino acids (circular peptide) [8, 16].

### 1.2 PROBLEM ASSESSMENT

Analysis of operational data of five major surface water treatment plants in the Netherlands has been performed, of which a representative cross-section is given in Table 1.1 [19]. These all produce water for different purposes (drinking water, industrial water and dune infiltration water), and face growing problems caused by algae. They are interested in efficient short- and long-term
Microcystis aeruginosa Removal by Dissolved Air Flotation (DAF)

treatment strategies and process modifications to address the algae problem. The enterprises are North Holland Water Supply Companies (PWN), Rhine-Kennemerland Water Transport Company (WRK), Dune Water Supply Company South Holland (DZH), Amsterdam Water Supply (GWA) and Energy and Water Supply Company Rhineland (EWR). At a later stage of the research after the further presented analyses were completed, two more enterprises with similar interests were involved, namely Water Supply Association Overijssel - Regio Oost (WMO, formerly Water Supply Company Oost-Twente - WOT), and Groningen Water Supply Company (GWG) (Fig. 1.1).

Fig. 1.1 Locations of the water treatment plants of the seven water treatment enterprises.

Although the origin of all concerned surface water is in essence river Rhine or Meuse water, the water quality in the five sources largely varies, because abstraction is almost never practised directly from the rivers. GWA treats water from the Loenderveen Lake, which is regularly replenished with Bethune polder drainage water (in the future to be mixed with Amsterdam-Rhine canal water at a ratio of 1:1). PWN and WRK treat water from the IJssel Lake, which is fed with water from river Rhine via one of its branches, the IJssel river. DZH practices dune infiltration of water abstracted from the Andels Meuse (a dammed arm of river Meuse, practically serving as a reservoir), and EWR of Rhineland polder drainage water. The purpose of their treatment also varies (drinking water, industrial water, water for dune infiltration, etc.) and so does the water treatment technology applied. Table 1.5 summarises the selected water quality management and treatment technology.
**Table 1.1** Year-average minimum and maximum water quality of surface water resources, based on average monthly measurements by the water enterprises.

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>IJssel Lake (Reservoir)</th>
<th>IJssel Lake (Reservoir)</th>
<th>Loenderveen Lake</th>
<th>Andels Meuse GWA</th>
<th>Andels Meuse Den Haag</th>
<th>Polder Water Katwijk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>1.2-20.7</td>
<td>1.4-20.3</td>
<td>3.6-22.3</td>
<td>1.8-22.4</td>
<td>1.5-21.6</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.9-9.45</td>
<td>7.7-8.9</td>
<td>7.5-8.4</td>
<td>7.7-8.6</td>
<td>7.6-8.5</td>
<td></td>
</tr>
<tr>
<td>PO₄&lt;sup&gt;3-&lt;/sup&gt; mgP/L</td>
<td>0.0077-0.095</td>
<td>0-0.014</td>
<td>0.006-0.063</td>
<td>0.124-1.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO₄&lt;sup&gt;-&lt;/sup&gt; mgP/L</td>
<td>0.06-0.76</td>
<td>0.05-0.25</td>
<td>0.007-0.04</td>
<td>0.04-0.2</td>
<td>0.39-1.15</td>
<td></td>
</tr>
<tr>
<td>NO₃&lt;sup&gt;-&lt;/sup&gt; mgN/L</td>
<td>N.M.</td>
<td>0.57-4.52</td>
<td>0.42-1.44</td>
<td>1.74-5.5</td>
<td>1.1-6.6</td>
<td></td>
</tr>
<tr>
<td>NH₄&lt;sup&gt;-&lt;/sup&gt; mgN/L</td>
<td>0.04-0.79</td>
<td>0.04-0.9</td>
<td>0.12-0.89</td>
<td>0.08-0.55</td>
<td>0.17-2.78</td>
<td></td>
</tr>
<tr>
<td>SiO₂&lt;sub&gt;2&lt;/sub&gt; mgSi/L</td>
<td>N.M.</td>
<td>0.05-2.8</td>
<td>3.7-13.1</td>
<td>0.25-5.6</td>
<td>1.04-11</td>
<td></td>
</tr>
<tr>
<td>Chl a µg/L</td>
<td>8.6-198</td>
<td>6.5-101</td>
<td>1.3-8.4</td>
<td>1.6-37</td>
<td>1.5-51</td>
<td></td>
</tr>
<tr>
<td>Chl t µg/L</td>
<td>18-238</td>
<td>13-132</td>
<td>2.7-10.3</td>
<td>2.6-58</td>
<td>N.M</td>
<td></td>
</tr>
<tr>
<td>Algal Vol. mm&lt;sup&gt;3&lt;/sup&gt;/L</td>
<td>1.1-411</td>
<td>0.4-97</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
</tr>
</tbody>
</table>

Chl a : Chlorophyll-<i>a</i>  PO₄<sup>-</sup>: ortho phosphate  N.M.: not measured  
Chl t : Chlorophyll-total  PO₄<sup>-</sup>: total phosphate

During the collection and processing of the data, it appeared that the degree of attention paid to algae, as demonstrated by the frequency and diversity of algae related measurements, varies between the enterprises, and is proportional to the number of problems experienced in the past. The attention is determined, for example, by whether the end product is drinking, industrial or infiltration water. This inconsistency in the data set is compounded by the absence of a proper algae related standard for product water, and by the absence of a proper measuring technique that is able to include all types of algae in proportion to their actual concentrations.

Statistical analysis of the data related to comparison of the five water resources was performed. The aim of the two way analysis of variance (ANOVA) was to test the similarity between the (year-average) raw water quality of the five water resource localities, and to check whether the raw water quality of each of the water resources has changed within the analysed time period (see Table 1.1). The results show: (i) significant differences between the raw water quality at the five localities (raw water resources), and (ii) no significant changes of the water quality of each of the localities during the analysed periods. Based on a multiple range test, Table 1.2 reflects the similarities for the analysed water quality parameters at different localities.
Table 1.2  Similarity of raw water quality between the five locations. a, b, c, d denote typical water quality categories, based on the two way ANOVA.

<table>
<thead>
<tr>
<th>Local</th>
<th>t</th>
<th>pH</th>
<th>PO₄₋₀</th>
<th>PO₄₋₄</th>
<th>NO₂₋₄</th>
<th>NH₄</th>
<th>SiO₂</th>
<th>Chl-α</th>
<th>Chl-τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ab</td>
<td>c</td>
<td>N.M.</td>
<td>c</td>
<td>N.M.</td>
<td>a</td>
<td>N.M.</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>4</td>
<td>bc</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>c</td>
<td>ab</td>
<td>N.M.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>c</td>
<td>ab</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
</tbody>
</table>

1 - PWN reservoir  3 - DZH Andels Meuse  5 - GWA Loenderveen Lake
2 - WRK III reservoir  4 - EWR polder water

N.M.: no measurements
available for the locality

Chl a: Chlorophyll-a
Chl t: Chlorophyll-total
NO₂₋₄ : nitrites + nitrates

Multiple correlation analysis of the variables (analysed raw water quality parameters) for all the localities (raw water resources) shows high correlation coefficients between chlorophyll-tot on one hand and pH, ortho-PO₄, total PO₄, NO₂ + NO₃, and SiO₂ on the other, and low correlation coefficients between chlorophyll-tot and t and NH₄ (Table 1.3). The lack of data for SiO₂ for the polder water may explain to some extent the high negative correlation coefficient obtained.

Similar correlations were obtained for chlorophyll-a. Based on the maximum correlation coefficients, simple and multiple linear regression analyses were carried out, showing highest r² values for simple linear regression between log(chlorophyll-tot) and log(PO₄₋₄) [ r² = 0.87], and for multiple linear regression between log(chlorophyll-a), log(PO₄₋₄) and pH [ r² = 0.80]. Fig. 1.2 represents a plot of the observed versus the predicted log(chlorophyll-a) values in function of the phosphate concentration and pH. The transformation equation predicting the (chlorophyll-a) value on a year-average maximum basis is: pr.log(chlorophyll-a) = 0.52 log(PO₄₋₄) + 0.6(pH) - 3.2. The highest r² values for PO₄-tot suggest that phosphorus is the key element which controls algae growth in surface water impoundments, consistent with the conclusions of Vollenweider [20] and also elaborated by many authors like Sakamoto [21], Dillon and Rigler [22], and Tillman et al. [23], for water impoundments under a range of conditions.

Table 1.3  Correlation coefficients (r) and significance levels (P) for correlation of log (chlorophyll-tot) with log values for different variables (except for pH which is a log value itself). Number of data n = 15.

<table>
<thead>
<tr>
<th>Coef.</th>
<th>t</th>
<th>pH</th>
<th>PO₄₋₀</th>
<th>PO₄₋₄</th>
<th>NO₂₋₄</th>
<th>NH₄</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>0.11</td>
<td>0.76</td>
<td>0.96</td>
<td>0.93</td>
<td>0.81</td>
<td>-0.09</td>
<td>-0.8</td>
</tr>
<tr>
<td>P</td>
<td>0.7</td>
<td>0.0011</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0002</td>
<td>0.75</td>
<td>0.0003</td>
</tr>
</tbody>
</table>
\[ \text{pr.} \log(\text{chl-a}) = 0.52 \log(\text{PO4-i}) + 0.6 \times (\text{pH}) - 3.2 \]

**Fig. 1.2** Observed versus predicted \( \log(\text{chlorophyll-a}) \) values, \( r^2 = 0.8 \).

The reservoirs' chlorophyll and phosphorus data were superimposed on a graph by Harris [24] (based on results for a combination of lakes analysed by Janus and Vollenweider, and a number of oligotrophic Canadian lakes); the results fall in the 95\% confidence limit of the regression line (Fig.1.3).

**Fig. 1.3** Annual mean chlorophyll vs. P concentrations for the five impoundments, superimposed on a graph from Harris [23].
The close relation between chlorophyll-\(a\) and phosphorus, emerging from the multiple regression analysis, suggests causality and is again in accordance with Vollenweider's results. However, the causal relation between chlorophyll-\(a\) and pH is more complex. Although high correlation coefficients do not automatically imply the presence of causal relations, the causal relation between chlorophyll-\(a\) and pH may be supported by the CO\(_2\)/pH relation hypothesis. Indeed, the relatively high pH of the five impoundments (pH 7.5-9.45 on year average basis) favours the growth of cyanobacteria at high eutrophication levels [25], as recorded in our case [19]. In addition it may be hypothesized that a feedback mechanism exists between chlorophyll, PO\(_4\) and pH, in the sense that resuspension of phosphorus from reservoir sediments occurs under the recorded high pH conditions, which supports further algae growth [26, 27].

The intensive photosynthetic activity of high biomass concentrations further shifts pH to high values, possibly to the point where C becomes a limiting factor. As cyanobacteria have lower saturation constants \(K_m\) for uptake of total carbon and CO\(_2\), this condition combined with the high pH promotes cyanobacteria dominance [25].

Summaries of the observations on the most significant species encountered in the five impoundments describing their characteristics and treatability, are presented in Table 1.4. The treatability of the algae species, i.e. the extent of their removal in water treatment, is mainly affected by (i) the treatment technology applied, (ii) optimization of the applied treatment technology, and (iii) characteristics of the algal species involved. Although the choice of the treatment technology rarely is made on the basis of efficient algae removal alone, the occurrence of the periodical algae blooms plays an important role. Under normal circumstances (moderate algae concentrations) algae can be removed more or less efficiently by commonly applied treatment technologies.

However, this technology is not necessarily optimal for the removal of all the algae species concurrently or separately (at other time periods) present in the water. The algae characteristics and properties influence their removal, including size, shape, cell surface characteristics (composition of algal cell wall and resultant colloidal surface charge characteristics), excretion of EOM and motility. Many of these characteristics vary with algae age, as well as within subspecies, limiting the removal predictability. In this light, the terms 'Problematic', 'Good', etc. treatability of Table 1.4 are only indicative. They are used to characterize the general degree of problems related to a particular algal species removal, the effect on effluent water quality, and the water production costs.

Each of the studied water impoundments is characterised by seasonal (yearly) variations. Algal blooms are common during certain periods of the year, but they are proportional to the degree of eutrophication and most acute in the cases of WRK (Figs. 1.4 and 1.5) and PWN treating IJssel Lake water. A pronounced seasonal occurrence of cyanobacteria (especially \(M. \text{aeruginosa}\)) is found in all five water resources, again showing proportionality between concentration and the degree of eutrophication. This was found to be most typical in Loenderveen Lake. While diatoms are characterised as superior competitors under phosphorus limitation (high N/P ratio) and water temperature below 14°C, green algae and cyanobacteria are dominant under nitrogen limitation (low N/P and Si/P ratios) and high temperatures [23].
Table 1.4 The most significant algae species encountered in the five impoundments, indicating their basic characteristics and treatability.

<table>
<thead>
<tr>
<th>Algae species and taxonomy</th>
<th>Figurative representation</th>
<th>Characteristics</th>
<th>Treatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melosira spp. (Diatomeae)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Porous, capsule like, cylindrical cells forming filaments; blooms; ( L=10-40 \mu m; W=5-20 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Stephanodiscus spp. (Diatomeae)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Single, porous cells, spines at edges; in hard waters or basic lakes; ( L=8-20 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Asterionella spp. (Diatomeae)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Often very abundant, spoke like arrangement of rectangular frustules; in hard waters; ( L=40-130 \mu m; W=2 \mu m ).</td>
<td>Moderately problematic</td>
</tr>
<tr>
<td>Nitzschia spp. (Diatomeae)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Commonly solitary frustules, tapered at ends, straight or sigmoid, porous; ( L=25-110 \mu m; W=5-10 \mu m ).</td>
<td>Moderately problematic</td>
</tr>
<tr>
<td>( \mu )-algae (Diatomeae)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Small capsule like cylindrical cells, very much like Stephanodiscus hantzschlii.</td>
<td>Problematic</td>
</tr>
<tr>
<td>Microcystis spp. (Cyanophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Irregularly shaped colonies of thousands of sphere cells, also single cells; gas vacuoles ( (N_2);extensive blooms-surface mat; D=3-7 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Oscillatoria spp. (Cyanophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Cells forming filaments - solitary or intermingled, cells lack definite sheath; blooms; ( L=2-4 \mu m, (L_a=100 \mu m); W=3-5 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Aphanothecophora spp. (Cyanophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Cells forming filamentous bundles, heterocysts present; blooms; ( L=5-15 \mu m, (L_a=150 \mu m); W=5-6 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Anabaena spp. (Cyanophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Cells forming filaments, heterocysts present; upper layers; blooms - surface mats; ( L=6-8 \mu m, (L_a=30-35 \mu m); W=6 \mu m ).</td>
<td>Problematic</td>
</tr>
<tr>
<td>Scenedesmus spp. (Chlorophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>4, 8 or 12 oval or fusiform cells forming colonies, 1 or 2 spines at end cells; ( L=10-15 \mu m ).</td>
<td>Moderately good</td>
</tr>
<tr>
<td>Coelastrum spp. (Chlorophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Spherical or polygonal cells forming hollow colonies, by protuberances from mucilaginous sheaths; ( D=8-12 \mu m ).</td>
<td>Moderately good</td>
</tr>
<tr>
<td>Oocystis spp. (Chlorophyta)</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Elliptic or lemon shaped, one or more generations of mother cell walls enclose daughter cells; ( L=14-26 \mu m; W=10-20 \mu m ).</td>
<td>Good</td>
</tr>
<tr>
<td>Cryptophyecae spp.</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Solitary cells, rarely colonial, protozoan like, 2 flagella, chloroplast pigments - brown, blue or red.</td>
<td>Moderately problematic</td>
</tr>
<tr>
<td>Chrysothecae spp.</td>
<td><img src="image" alt="Figurative representation" /></td>
<td>Unicellular or colonial, rarely filamentous, chloroplast pigments - yellow, brown, golden brown, thick wall, 1 or 2 flagella, motile.</td>
<td>Moderately problematic</td>
</tr>
</tbody>
</table>

1. - PWN reservoir  
2. - EWR polder water  
3. - GWA Loezanderveen Lake;  
4. - WRK III reservoir  
5. - Andels Meuze.  
L - cell length  
\( L_a \) - total length of filament  
W - cell width  
D - cell diameter  

Comment: The morphology of different algal species asserts the need of different algae counting procedures. Microcystis aeruginosa is counted as single cells and as colonies. Bundles of filamentous species most often disintegrate during the preparation of the sample; an attempt is made to count all the algae that may form such bundle structures. Scenedesmus spp. of 8 or 12 cells are counted as 2 or 3 Scenedesmus entities. Similarly other disintegrated colonial species are counted as separate entities.
Fig. 1.4  Average monthly algal count for the WRK III reservoir (integrated over the total reservoir depth of 20 m), for different algal taxa in the period 1988-92.

Fig. 1.5  Average yearly algae count for different taxa in the WRK III reservoir for the period 1988-92.

Reservoir management involving chemicals application (affecting nutrients availability, pH, etc.) and water mixing within the reservoir, as well as climatic conditions, influence the phytoplankton composition as for example in the PWN and WRK reservoirs where higher
concentrations of *Oscillatoria* spp. were found in the period of 1990-92. This is consistent with other experiences under Dutch climatic circumstances [25]. This suggests that the current raw water quality criteria are insufficient to avoid prolonged cyanobacteria blooms. Cyanobacterial dominance refers to a high biomass concentration, which is correlated (indirectly) to the nutrient level. This is the case in particular with *Oscillatoria* spp., while for *Microcystis* spp. it is the limiting nutrient that most likely will determine the magnitude of its bloom.

1.3 DISCUSSION

1.3.1 Algae and water treatment - problems and remedies

1.3.1.a Reservoir management

To cope with algae efficiently requires a combination of detailed water quality monitoring, reservoir water quality management, and water treatment measures. Appropriate and especially well timed microbiological analysis (i.e. done immediately after sampling and not postponed for weeks, which often is the practice), accompanied with other physio-chemical analysis provides a better tool for prediction of algae concentration and species variations. Although treatment plant operators are found to be increasingly aware of the importance of the prediction capacity, it often is neglected or insufficiently addressed. Delays between sampling and analysis typically result in poor treatment process operation. On the other hand, it is generally very effective to reduce the algal load ahead of the treatment through reservoir water quality management and pretreatment as it appears that no treatment step on its own is able to ensure adequate removal rates. A range of reservoir management techniques are applied in this context with varying degrees of success: phosphorus removal (either by precipitation with coagulant, or by diverting phosphorus contributing flows), artificial destratification by mixing of the water column, use of algicides (mainly copper sulphate), sonic disruption of algal cells, suction dredging, and aeration of the hypolimnetic layer [4]. Reservoir management significantly diminishes the algae load, but the appropriate approach is reservoir and algae specific.

The successful application of better reservoir design is the case presented in Fig. 1.6. The use of the shallow 3 m deep PWN reservoir was temporarily supplemented by the 20 m deep WRK III reservoir, resulting in drastic reduction of the exposure to sun-light and subsequent poor algae growth. Examples of successful pre-treatment include the coagulation with ferrous sulphate and settling of water entering the water reservoir of GWA, the application of ferrous sulphate in Andels Meuse by DZH and in the WRK III reservoir (which also includes periodical mixing of the water column). On the other hand, such measures have also been reported to yield adverse effects. In the Wahnbachtalsperrenverband in Siegburg, Germany, phosphorus reduction in the raw water reservoirs led to a rapid increase in diatom level at the expense of other algae, and resulted in poorer overall treatment performance during periods of their blooms.
Fig. 1.6  Average algal volume for different taxa in the reservoirs of PWN (3 m deep) and WRK III (20 m deep), (1987 data unavailable).

1.3.1.b Treatment process

Cyanobacteria and in particular *Microcystis* spp. and *Oscillatoria* spp. are known to pass readily through treatment and end up in drinking water in relatively large numbers. A critical feature of the *Microcystis* spp. is their ability to form colonies, as well as to exist in a single cell form, whilst *Oscillatoria* spp. can exist as solitary or intermingled filaments. Small algae pass through filters more readily than larger ones so that when blooms of small algae, such as *Microcystis* spp. occur, their counts in treated water are high especially towards the end of the bloom period when colonies disintegrate naturally, or as a consequence of algicides. Up to $5.3 \times 10^4$ cells/mL of the former and $4.5 \times 10^4$ cells/mL of the latter species have been recorded by the Severn Trent Water Authority in 1985 and 1986 in the United Kingdom, for filtered water [4]. *Microcystis* spp. cells can rupture and leak intra-cellular substances during turbulent aqueduct transport from the reservoir to the treatment site (rupture rate between 61-72%) [28]. Similar rupture and colony break-up may be expected during initial pumping stages in water treatment plants, representative for Dutch operation circumstances. In other words, water treatment plant design may in itself aggravate the algae related problems.

In general, the treatment approach in the studied plants is complex and aims at the overall removal optimization of different pollutants, including suspended solids, dissolved and colloidal matter, organic micropollutants, heavy metals, algae, etc.; this varies depending on the raw water source as well as the final product user (Table 1.5). Coagulation and flocculation, and rapid sand filtration are applied in all plants, while granular activated carbon filtration is used in three cases (GWA, WRK and PWN). Dissolved air flotation is applied at DZH and EWR, while sedimentation is practised at WRK III and PWN. Slow sand filtration is practised only at the GWA.
Table 1.5 The treatment processes in the five studied treatment plants.

<table>
<thead>
<tr>
<th>MANAGEMENT &amp; TREATMENT TECHNOLOGY APPLIED</th>
<th>GWA 30 Mm³/y</th>
<th>WRK III 110 Mm³/y</th>
<th>PWN 35 Mm³/y</th>
<th>DZH 70 Mm³/y</th>
<th>EWR 15 Mm³/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weesperkarspel</td>
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<tr>
<td>Princes Juliana</td>
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<td>Andijk</td>
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<tr>
<td>Bergambacht + Scheveningen</td>
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<tr>
<td>Lindenbergh</td>
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<tr>
<td>pre-coagulation</td>
<td>###</td>
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<tr>
<td>pre-settling</td>
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<td>reservoir</td>
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<td>reservoir mixing</td>
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<tr>
<td>pre-filtration</td>
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<tr>
<td>straining 35µm</td>
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<tr>
<td>sieves 200µm</td>
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<tr>
<td>pre-chlorination</td>
<td>#P#</td>
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<td>#P#</td>
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<td>transport Cl₂</td>
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<td>ozone</td>
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<tr>
<td>softening</td>
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<tr>
<td>coagulation/flocculation</td>
<td>ooo</td>
<td>###</td>
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<td>###</td>
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<tr>
<td>sedimentation</td>
<td>ooo</td>
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<tr>
<td>flotation (DAF)</td>
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<tr>
<td>rapid sand filters</td>
<td>ooo</td>
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<tr>
<td>activated carbon</td>
<td>#o#</td>
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<tr>
<td>slow sand filters</td>
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<tr>
<td>straining 30µm</td>
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<tr>
<td>post-chlorination</td>
<td>#P#</td>
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<tr>
<td>CIO₂ disinfection</td>
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</tr>
</tbody>
</table>

### - PRESENTLY IN OPERATION  ooo - PREVIOUSLY IN OPERATION  #P# - PERIODICALLY APPLIED  #o# - REPLACED WITH (IN OPERATION NOW)

Algal blooms and typically those of cyanobacteria, pose the most serious treatment problems. These include: (i) interference with the coagulation and flocculation process, (ii) increased disinfectant demand, (iii) trihalomethane production, (iv) frequent filter blocking, and (v) increased use of backwash water (Table 1.6). This translates into higher production cost. Process modifications to address these problems can also be expensive or have side effects. As no algae standards or objectives exist, water companies tend to deal with the problem on the basis of 'as much as possible' removal, within the technological context and production cost bracket that is considered commonly acceptable. This approach is usually indiscriminatory and poorly focused. Local guide levels exist such as those at the Wahnachtalsperrenverband in Siegburg, Germany [29], (0.1 µg/L chlorophyll-a in treated water).
Table 1.6

Present and anticipated situation in the five studied Dutch water enterprises. Most significant alga species encountered, related treatment and distribution problems, and remedies (illustrations from [30], except for GWA photo material of μ-algae deposits on GAC filter).

<table>
<thead>
<tr>
<th>Company</th>
<th>Raw water source, treatment plans and process</th>
<th>Characteristic algal species in water resources</th>
<th>Present situation with respect to raw water source and treatment</th>
<th>Anticipated development</th>
</tr>
</thead>
</table>
| PWN     | IJssel Lake-Andijk                          | Microcystis spp. (Cyanophyta)  
-Straining 35 μm  
-Cl<sub>2</sub> 6 g/m<sup>3</sup>  
-FeCl<sub>3</sub> 16 g/m<sup>3</sup>  
-Ca(OH)<sub>2</sub> 30.5 g/m<sup>3</sup>  
-Polyelect. 0.5 g/m<sup>3</sup>  
-SED, v=3.5 m/h  
-RSF, v=10 m/h  
-GAC, v=13.5 m/h  
-Straining 35 μm  
-ClO<sub>2</sub> | Serious current operational difficulties:  
-100% coagulant and coagulant aid dose increase (up to 40mg/l Fe<sup>3+</sup> and 1.0 mg/l polyelectrolyte)  
-tribhalomethane formation  
-increased backwash water quantity  
-algae passing through treatment | In long term only partial improvement of present eutrophication of raw water resource expected  
-Partial improvement of situation due to deepening of reservoir before treatment |
| WRK     | IJssel Lake-Princess Juliana, Andijk        | Microcystis spp. (Cyanophyta)  
-Straining 200 μm  
-Fe<sub>2</sub>SO<sub>4</sub> 30 g/m<sup>3</sup>  
-Polyelect.-0.2 g/m<sup>3</sup>  
-SED (lamella)  
-RSF, v=10 m/h  
-GAC (partial) | Serious current operational difficulties:  
-100% coagulant and coagulant aid dose increase (up to 40 g/m<sup>3</sup> Fe<sup>3+</sup> and 1.0 g/m<sup>3</sup> polyelectrolyte)  
-tribhalomethanes formation  
-increased backwash water quantity  
-algae passing through treatment  
-increased MFI and AOC values and possible infiltration wells clogging | In long term only partial improvement of present eutrophication of raw water resource expected  
-Partial improvement of situation due to mixing and coagulant application in reservoir |
| GWA     | Loenderveen Lake-Waaporkarpsel              | Microcystis spp. (Cyanophyta)  
-Straining 200 μm  
-Fe<sub>2</sub>SO<sub>4</sub> 30 g/m<sup>3</sup>  
-Polyelect.-0.2 g/m<sup>3</sup>  
-SED (lamella)  
-RSF, v=10 m/h  
-GAC  
-SSP | Operational difficulties:  
-surface clogging of GAC filters by phytoand zooplankton cake layer  
-increased backwash water quantity  
-algae passing through treatment  
-increased MFI and AOC values and possible infiltration wells clogging | New surface water source of inferior quality (contributing to eutrophication) to be used to double production capacity  
-Reduction of algae load over GAC filters due to:  
-direct filtration mode of filtration plant at intakes (1-3 g Fe<sup>3+</sup>/m<sup>2</sup>)  
-reduced ozone doses at beginning of process |
| DZH     | Andels Meuse-Bergambacht + Scheveningen    | Microcystis spp. (Cyanophyta)  
-Straining 200 μm  
-Fe<sub>2</sub>SO<sub>4</sub> 30 g/m<sup>3</sup>  
-Polyelect.-0.2 g/m<sup>3</sup>  
-SED (lamella)  
-RSF, v=10 m/h  
-GAC  
-SSP | Operational difficulties:  
-algae and cellular products passing through treatment  
-increased AOC values, resulting in reduced pipe flow due to increased k-values of pipes  
-increased backwash water quantity  
-algae passing through treatment  
-increased MFI and AOC values and possible infiltration wells clogging | Unchanged situation as long as application of phosphate precipitation in Andels Meuse is allowed  
-New direct filtration plant for algae removal in Brekel under investigation |
| EWR     | Rhineland polder water-Lindenbergh          | Microcystis spp. (Cyanophyta)  
-Straining 200 μm  
-Fe<sub>2</sub>SO<sub>4</sub> 30 g/m<sup>3</sup>  
-DAP, t=15 min  
-RSF, v=5 m/h | Product water quality problems:  
-algae passing through treatment in large quantities, especially during periodical blooms  
-increased backwash water quantity  
-algae passing through treatment  
-increased MFI and AOC values and possible infiltration wells clogging | Complete change of present raw water source with one of better quality, possibly Andels Meuse |

RSP - rapid sand filtration;  
SSP - slow sand filtration;  
DAF - dissolved air flotation;  
GAC - granular activated carbon  
SED - sedimentation;  
PAC - powder activated carbon
Nevertheless, their implementation on a wider scale and at different circumstances is not always feasible. It has been argued that the discussed chlorophyll-α guide level is too stringent in view of the very low assimilable organic carbon (AOC) value associated with it [31]. Namely, the proposed 0.1 μg/L chlorophyll-α guideline value should imply 3 μg/L AOC, which is lower than the already ambitious recommended 10 μg/L AOC required for biologically stable water (proposed by van der Kooij [32]).

Research in the past two decades was mostly directed at optimising conventional treatment processes, commonly centred around sedimentation and filtration. Agglomeration (coagulation/flocculation) has received the largest attention, as it is the prerequisite for any efficient particles (and algae) removal regardless of the subsequent down-stream removal process (sedimentation, flotation or filtration). Efficient water conditioning with the purpose of improving the coagulation/flocculation process was approached in a similar manner. However, it was soon realised that it is typically impossible to achieve adequate algae removal when they are present in concentrations that are typical for some eutrophic reservoirs (periodically up to 10^8 - 10^9 cells/mL). Obtained removal rates strongly depend on prevailing plankton type and range from 50-99.9%. However, even a rate of 99.9% removal can still be inadequate for raw water of such poor quality [29].

1.3.2 Dissolved air flotation (DAF) - a viable solution option

Because of the natural tendency of algae to float dissolved air flotation (DAF) attracts attention as a (pre)treatment option prior to final filtration. Because DAF requires a preceding particle agglomeration (coagulation/flocculation) step, it performs equally well as common flocculation/sedimentation with respect to DOC, UV, true colour and trihalomethane precursor removal [33, 34]. On the other hand DAF tends to be more efficient than sedimentation for removal of turbidity and particulates formed by coagulation [35]. Experience from newly built flotation facilities for drinking water treatment (e.g. Birmingham Frankley, UK; Millwood New Castle, USA; Pietarsaari, Finland), and from adapted existing plants, where e.g. sedimentation was replaced by flotation followed by rapid sand filtration document this [36, 37]. It is generally confirmed that algal removal efficiency can be substantially enhanced by flocculation and flotation upstream of the final filtration. The same applies for algae conditioning, i.e. bringing the algae into a state which results in their more efficient down-stream process removal, by application of oxidants, e.g. ozone [38], or KMnO₄ [39].

Janssens [40] has proposed a tentative diagram to be used for process selection based on raw water turbidity and algal content (Fig.1.7). If all other quality requirements are fulfilled regarding DOC, hardness, colour, etc., flotation is the best available (pre)treatment technology for treatment of raw water with chlorophyll-α values of typically > 10 μg/L. This is the case in all of the five studied companies for shorter or longer periods of the year (Table 1.1). In addition, under the Dutch circumstances the occurrence of M. aeruginosa (Table 1.4) favours use of DAF, because this species is characterised by buoyancy [3], which renders them more susceptible to removal by the rising air bubbles in DAF.
Fig. 1.7 Typical selection diagram for a water treatment process based on turbidity and chlorophyll-α concentration (from Janssens [40]).

Although this diagram can be very useful, it does not consider a range of factors which may be of substantial impact on the choice of process technology. Such factors include algae morphology and physiology (different species exhibit different response to treatment) [41], the source and character of turbidity, temperature, colloidal and particulate matter concentration, and possibly other factors as well. Furthermore, the choice of technology is largely a matter of cost-benefit analysis, suggesting that this diagram can be considered only as indicative.

A typical layout of a DAF treatment plant is presented in Fig. 1.8. It consists of a tank in which two zones are distinguished: (i) the contact zone, and (ii) the separation zone.

Fig. 1.8 Schematic presentation of a DAF treatment plant [42].
In DAF, air is introduced into the contact zone via a pressurised (approximately 500 kPa) recycled stream of treated water (5-10% of total flow). The change of pressure from e.g. 500 kPa to atmospheric results in the production of numerous microscopic (10-100 μm) air bubbles which attach to the particles (flocs). The commonly large ratio between air bubble and particle concentration of $10^2-10^3$, encountered in normal surface water treatment, is suggested responsible for the high DAF efficiency [42]. The particle-bubble agglomerates rise to the surface in the separation zone, where they are easily skimmed off as a light foam.

The following advantages of DAF are proposed [43]:

- small surface needed for unit and equipment;
- low civil engineering cost requirements;
- typical reduction of 10-20% in chemicals consumption as compared to conventional sedimentation;
- high dry solids content of the sludge (4-6%), compared to sedimentation (2-4%);
- lower water losses (1%, compared to 3% for sedimentation) due to production of sludge with a higher solids content;
- less affected by flow variations;
- suitable for intermittent use, reaching steady quality after approximately 60 min;
- operates in cold climates with minimum flotation time less than 10 min, and less sensitive to temperature variations than sedimentation;
- high algae removal efficiency.

Disadvantages include higher operational costs and the requirement to have skilled operating personnel. Nevertheless, for treating water with high algal count and relatively low turbidity DAF appears to be the most cost-effective technology. Water with high turbidity, on the other hand, is also treatable to a certain limit and with appropriate process modifications.

1.3.3 Agglomeration (coagulation/flocculation) of algae

The single collector collision efficiency DAF kinetic model proposed by Malley and Edzwald [45] recognises two sets of variables that define process efficiency:

- pre-treatment variables ahead of the flotation tank, which influence the particle-bubble attachment efficiency, the particle concentration and the particle-bubble collision efficiency;

- design and operation variables within the flotation tank, which influence the bubble size and concentration.

The agglomeration (coagulation/flocculation) step is a critical part of the DAF; it therefore deserves to receive priority in comprehensive research approach. Such comprehensive optimisation should take into account the down-stream filtration. Neither conventional sedimentation, nor advanced DAF are able to remove on their own the number of algae encountered in eutrophied surface water. Model calculations suggest that the particle destabilization degree is more important than the floc size [42]. pH and coagulant dose that
produce floc particles with little or no charge, generally result in favourable flotation conditions. Particles (algae) must be destabilized for good particle attachment to bubbles, as algae stability is caused mainly by: (i) the electrostatic repulsive force due to the negative surface charge (at pH 2.5-11.5), and (ii) the steric hindrance due to the water layer associated with hydrophilic surface and the adsorbed EOM at the cell surface [42]. Bernhardt and Clasen [45] conclude that algal cells can be considered to behave as inert particles and that the classical coagulation theory therefore is applicable; algae could be destabilized, aggregated and thus brought into filterable form, by adsorption coagulation or sweep coagulation. This can be achieved by charge neutralization by means of adsorption of positively charged organic or inorganic polyelectrolytes, or by metal hydrolysates when sweep coagulation is applicable. Agglomeration conditions that produce particles with little or no charge generally result in efficient DAF [42]. The selection of inorganic or organic coagulants as sole coagulants or coagulant aids, pH, and other coagulation variables therefore need further study.

The kinetic variables (G and t values) for efficient mixing and coagulation, as well as flocculation (i.e. creating particle collision opportunities) similarly need to be optimised. Unlike mixing and coagulation which take place almost instantly after coagulant addition (floc formation starts within $10^2$ s up to a few seconds), the floc formation requires lower mixing energy input (low G) during longer time periods (5-20 min), enabling particles to collide. In practice, floc formation and floc break-up occur simultaneously, making application of mechanistic models complicated. However, floc size and strength determine overall efficiency in the floc removal step. While efficient sedimentation requires larger, heavier and easily settleable flocs, the floc size of 10 μm to few tens of micrometer has been shown to be optimal for flotation [42, 44]; similar to filtration, flotation efficiency worsens for particle size of 1 μm and is one to two orders of magnitude lower for particles < 1 μm. Floc growth spurs initially by the presence of small but numerous primary particles, and thereafter it is determined by the collision of 'micro-aggregates'. In case of adsorption coagulation, as floc size increases, the number of polyelectrolyte bridges per particle decreases proportionally to floc size and the floc becomes weaker and more susceptible to shear by hydrodynamic forces.

Algal cell aggregates in particular appear to be susceptible to shear and hence turbulence. A shear-free transport of flocculated algae to further treatment is required. A critical location in DAF is the injection of the recirculated water through the injection nozzles or needle valves. Depending on the configuration of the DAF unit, flocs may be locally subjected to high shear. This suggests that longer flocculation times to produce larger flocs are questionable, if flocs break up anyway near the nozzles. Some authors [35] conclude that the flocculation time therefore does not affect flotation performance (based on turbidity measurements); good results can be obtained without flocculation or slow mixing, with flocs formation limited to the rapid mixing period of about 2 minutes. Others [46] suggest minimum flocculation time of 5-6 minutes. On the other hand, flocculation time e.g. at the Scheveningen flotation plant of DZH is in the range of 20-40 min, while in the Lindenbergh flotation plant of EWR it is 25 min.

Optimal agglomeration finally depends very much on the dominant algal species. Cyanobacteria appear in different sizes, shapes and forms, and differ in their EOM composition, which is known to influence the agglomeration process to a great extent. It can be expected that different species and seasonal conditions require different sets of optimal
agglomeration conditions for subsequent flotation. This calls for further study of the influence of morphological and physiological characteristics of alga species on the agglomeration and down-stream removal efficiency.

Particle (floc) characterisation such as automated particle count or computer image analysis becomes an essential tool in the assessment of the coagulation/flocculation and DAF process assessment.

1.3.4 Conditioning of algae

Recent advances in DAF operation pertain to the decrease of the flocculation and flotation time, and other process improvements related to the critical agglomeration (coagulation/flocculation) step. In addition, it was found that oxidants may under certain conditions (depending on raw water quality, coagulant dosage, location of dosing, etc.) improve coagulation and flocculation and hence down-stream floc removal efficiency. The positive experiences, especially with ozone [38, 47, 48] and KMnO₄ [39] in direct filtration, warrant further research on these oxidants prior to aggregation and DAF.

Although their use is not yet widespread, the application of oxidants as flocculation aid is becoming a viable option. In this context, the term conditioning seems appropriate to express the effect of oxidants on the algae structure and the resulting flocculation benefits. Namely, in addition to disinfection, secondary benefits arise from their effect on the surface chemistry of colloidal and suspended particles. As a consequence ozone can cause microflocculation (spontaneous flocculation), and hence coagulant dose reduction, improved water quality (measured as turbidity), and reduction in filter bed head-loss [47]. The mechanism of the induced flocculation is not yet fully understood; several mechanisms are proposed by Langlais et al. [49]: (i) reactions with algae, (ii) reduction of particle stability due to loss of adsorbed organic matter from natural particles, (iii) polymerization of natural organic matter (NOM), and (iv) break-up of metal-organic complexes yielding in situ iron production of metal coagulant.

The commonly recommended oxidant in DAF has been ozone, whether as a classical conditioner or for ozoflotation. Ozone reacts with the algal outer cells layer (EOM) and the algal cells themselves; the extent of oxidation depends on the algal species, making its effect seasonally dependent [38, 47]. Similarly, overdosing can break-up colonies, and damage cell structure. As one consequence, DOC and AOC levels may increase, as well as the toxins concentration [50, 51]. The optimization of the ozone dose for efficient aggregation and flotation, and the understanding of the process kinetics require further study. As an alternative KMnO₄ is not commonly applied as a disinfectant and little is known about its optimal use. Its efficiency as a conditioner is related to its oxidative activity and the coagulating effect of the hydrous manganese dioxide floc which is formed when the permanganate is reduced [39, 52].

Physical conditioning commonly consists of straining and its efficiency depends on algal size and shape. Microstraining is widely applied with mesh size usually in the range of 35 μm. Mesh sizes as low as 5 μm are commercially available, their application depends largely on
local raw water plankton and suspended matter concentration and composition. The experience in the five studied Dutch enterprises shows that microstrainers can substantially reduce the algal loads on the subsequent treatment step [19]. However, algae blooms often create problems in the operation of the microstrainers resulting in deteriorating effluent quality. Single cells of *Microcystis* spp. and *Oscillatoria* spp., although with distinctly different morphological features, have both been noted to pass through this treatment as in case of the WRK III and PWN treatment plant, causing increased algae counts in the final effluent. The current understanding of the role of this treatment step in the optimisation of the overall treatment scheme can benefit from further pilot studies.

Finally, the use of other physical conditioners such as UV light has not been considered to our knowledge. Its applicability as an efficient disinfectant is yet gaining increasing recognition [53]. UV light is not considered to be an efficient algicide as high dosages (~5000 J/m²) and long exposure times (several minutes) are probably necessary. Yet, its effect on the viability of algae and hence on aggregation and down-stream flotation, should position it as a potentially interesting research topic.

1.4 CONCLUSIONS

The problems related to the periodical high concentrations of algae, are assessed for five Dutch surface water treatment locations. Cyanobacteria, especially *M. aeruginosa* and *O. agardhii* are recognised as the most significant problem causing algae. Examples of efficient reservoir management including deep reservoir operation (WRK III and PWN since recently), coagulation/flocculation and settling within the reservoir (WRK III and DZH), periodical destratification mixing (WRK III), phosphate removal by coagulation/flocculation and settling prior to the reservoir (GWA), can substantially diminish the algae load on subsequent treatment. Water treatment plant managers and operators should carefully consider such positive experiences and investigate their applicability and feasibility in their circumstances. Nevertheless, high algae concentrations, and especially blooms, can still cause numerous treatment problems. This forces water companies to adapt short-term and long-term process modifications, which raises production costs. This raises the issue of further cost-benefit algae treatment optimisation, as well as the viability and applicability of advanced treatment technologies. Increase of the knowledge basis on these issues should improve treatment process operation and raise the confidence in the application of new more efficient technologies. Existing algae related treatment problems and recent research results suggest that there is still a large operational window for increasing the efficiency of existing treatment capacities, based on the cost-benefit principle.

Considering the natural tendency of algae to float, and the positive experiences elsewhere, dissolved air flotation emerges as an attractive treatment technology, as alternative to conventional sedimentation. It features a high rate, high efficiency, low chemicals consumption, and high versatility and adaptability. On the other hand, discrepancies exist between literature and practice, which suggests that optimisation would benefit from DAF further research. The fact that in the nineties many treatment plants in Western Europe will require an increase in production capacity (in our study GWA, DZH and GWG) due to
increased water consumption, or to upgrade the process efficiency due to more stringent water quality regulations, compound this opinion. DAF is also an attractive option to be considered as pre-treatment in combination with emerging membrane technology in case of high algal loads.

Research in the Netherlands should preferably focus on the process optimization of a comprehensive DAF-based treatment scheme for the removal of cyanobacteria species, notably *Microcystis* spp. and *Oscillatoria* spp. An integrated approach is preferred for this purpose, which includes the up-stream agglomeration (coagulation/flocculation) of particles, as well as down-stream filtration. The emphasis is to be placed on the agglomeration phase which is considered critical, whether of particles (algae) in the coagulation/flocculation stage or of particles (algae) and bubbles in the DAF stage. The effects of pre-treatment and conditioning steps on overall process efficiency should be assessed. Positive and negative side effects of the treatment must be assessed, especially with regard to the level of DOC and its AOC fraction in the effluent, because of the possibility of cell disruption by the oxidants. The same applies to the toxin levels in the effluent, which are considered a second priority, but are more difficult to quantify. Finally, the influence of algal morphology and physiology on the process mechanisms need to be investigated.

The evaluation of the process efficiency should be related to the kinetic parameters and rely on more comprehensive particle characterisation. This should include comparison of particle (floc) size frequency and volume distribution for raw water, for water subject to aggregation (coagulation/flocculation), and for treated water. Bubble size characterisation (size distribution) and particle charge related phenomena are also to be considered. This would enable characterisation of process efficiency in a qualitative and quantitative manner, and further clarify important aspects of process kinetics.

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Chapter 2

RESEARCH OBJECTIVES, HYPOTHESES AND METHODOLOGY

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2.1 Research scope and relevance

This research was initiated and sponsored by five Dutch water enterprises sharing the common problem of periodical algae blooms in their raw water resources - reservoirs:

-North Holland Water Supply Companies (Waterleidingbedrijf Noord-Holland-PWN),
-Rhine-Kennemerland Water Transport Company (Watertransportmaatschappij Rijn-Kennemerland- WRK),
-Amsterdam Water Supply (Gemeentewaterleiding Amsterdam-GWA),
-Dune Water Supply Company South Holland (Duinwaterbedrijf Zuid-Holland-DZH), and

During the research, the last two companies fused while the following two other Dutch enterprises with similar interests joined the research. The research was also joined and supported by Kiwa Research and Consultancy (Kiwa Onderzoek en Advies).

-Water Supply Association Overijssel - Regio Oost (Waterleiding Maatschappij Overijssel - Regio Oost-WMO, formerly Waterleidingbedrijf Oost-Twente-WOT),
-Groningen Water Supply Company (Gemeente Waterbedrijf Groningen-GWG).

The research started as a joint venture project between these companies, the Technical University Delft and the International Institute for Infrastructure, Hydraulic and Environmental Engineering, Delft, the latter taking the final responsibility for carrying out the research. The research progress was guided by staff members of the participating companies and academic/scientific institutions, through an Advisory Committee.

The first chapter studied the algae related problems and the treatment practice of the participating companies. This chapter gives an analysis of eutrophication and algae presence in the utilised water resources, it specifies water treatment problems, and it discusses short- or long-term treatment strategies. It also offers a short overview of current experiences from elsewhere with respect to coping with the algae problem in a cost effective manner, which served as a rationale for outlining the experimental part of the research.

Currently 32% of the total water production in the Netherlands originates from surface water bodies, each having a different degree of existing and forecasted eutrophication and algae problems. In all five studied cases periods of algal blooms were common. Some of the companies face the problem of highly eutrophied raw water resources (PWN, WRK), characterised by the tendency of phytoplankton population shift towards cyanobacteria species, which are most often responsible for seasonal blooms and particular treatment problems. Similarly, for the future increase of production capacity the GWA considers using a new surface water source (Amsterdam-Rhine canal water mixed with Bethune polder water at a 1:1 ratio) with higher eutrophication levels than the one currently utilized. Production capacity expansion is also planned by DZH, by increasing the abstraction from the currently utilised eutrophic source (pretreated Andels Meuse water). In case of the EWR, a complete change of the raw water source has occurred (River Meuse), caused partly by eutrophication and algae problems.

Although not a preferred alternative, surface water is expected to receive more attention in the
Netherlands in the future, due to restrictions on ground water use. This will carry the burden of coping with periodical algal blooms. Although water quality management and pollution control have considerably reduced eutrophication on most locations, more efforts are required especially in multinational rivers like the Rhine and the Meuse, and in lowering agricultural and diffuse pollution which are now the main causes of eutrophication. Being complex and costly, these protection programmes are still very difficult to apply in less developed countries, leaving them with growing eutrophication and water treatment problems. Despite all efforts, a moderate but visible degree of eutrophication is to remain with us.

The recent availability of efficient membrane technologies offers new avenues for treatment (PWN, GWA and GWG consider them for their extension programmes). Although successful ultrafiltration experiments without pretreatment (or including microstraining only) have been conducted in the Netherlands, one can predict that the impact of pretreatment, especially in case of high algal concentrations, will increase the productivity and the life time of the membranes. In the short term, existing constraints in conventional treatment call for treatment solutions such as:

- solving problems within the existing treatment technology structure (e.g. adjust coagulant dose or coagulation pH on a short term basis),
- modifying the existing technology structure (e.g. introduce an oxidant as a conditioner),
- retrofitting with more efficient treatment technology (e.g. an option to be considered is to replace existing sedimentation with DAF within the existing construction parameters),
- applying the most cost-efficient treatment technology for newly considered production capacities.

The natural tendency of algae to float, and several positive experiences in the Netherlands and elsewhere, make the dissolved air flotation (DAF) potentially attractive as an alternative to conventional sedimentation. DAF is nowadays practised at DZH, EWR and WMO (formerly WOT), while (lamella) sedimentation is practised by WRK and PWN. Consequently, the comparison of sedimentation and DAF, was identified as a priority research topic for the participating enterprises. The critical importance of the coagulation/flocculation process, as well as of down-stream filtration, calls for a comprehensive approach.

The application of oxidants (ozone and KMnO₄) as chemical conditioners is considered as a particularly important factor for improving the DAF process efficiency. The application of ozone and KMnO₄ is to be optimised and critically assessed in terms of their by-products. Similarly, the application of polyelectrolytes of different origin (natural or synthetic) and charge (cationic, anionic and non-ionic) will be assessed in the context of enhancing DAF efficiency. An attempt to qualify the involved process kinetic mechanisms will be made. This part of the research will provide deeper insight and knowledge over potentially valuable tools for improved algae removal within existing production capacity as well as for future expansion of existing plants.

To summarize, this research is intended to broaden and improve the understanding of conventional and advanced water treatment technologies, in the context of existing and expected algae, especially cyanobacteria related problems. Our previous analysis in Chapter 1 showed that these are the species which deserve our attention in terms of expected further eutrophication, as well as the amount of existing problems in treatment. It is intended to arm the participating companies with a firmer knowledge basis of their production capacities and provide tools for short
and long term algae problem solutions. It is expected to encourage their consideration and application of potentially beneficial chemical conditioning techniques of algae. Finally, it is to potentially contribute to the development of a rationale that would help define and quantify the 'algae problem', and help setting-up a standard in future.

2.2 Research objectives

Based on the previous discussion and chapter-wise supported rationale, the objectives of the research are:

- Optimize the process of agglomeration (coagulation/flocculation) of cyanobacteria (in particular Microcystis spp.) by metal coagulants (with or without the addition of organic or inorganic coagulant aids), under different coagulation and flocculation modes (G and t values), as a function of efficient water treatment centered on DAF, and to compare this with a treatment centered on sedimentation.

- Identify cyanobacteria (Microcystis spp.) characteristics that are process relevant, e.g. size, shape (form), cell surface properties, surface charge, EOM presence, etc.

- Assess and evaluate the benefits and the draw-backs of polyelectrolytes and oxidants, notably ozone and KMnO₄ for improved algae agglomeration (coagulation/flocculation) and down-stream DAF.

- Evaluate and contribute to the existing knowledge on DAF (and sedimentation) process kinetics; identify and assess qualitatively the influence of essential process parameters, the effect of coagulation/flocculation conditions on particle size and volume distribution, particle charge, and on resultant particle-bubble interaction. Similarly assess the impact of different process conditions on bubble characteristics and on resultant particle-bubble interaction.

- Evaluate and contribute to the existing knowledge on ozone and KMnO₄ algae conditioning process kinetics; identify and assess qualitatively the influence of essential process and water quality parameters, notably the effect of oxidant dose, organic matter concentration and composition, particle charge, etc., and their effect on resultant DAF efficiency.

2.3 Research hypotheses

The following hypotheses were developed to guide the experimental work and its design:

- Knowledge on the algal biology and ecology is necessary to understand and improve the removal process optimisation. The single celled M. aeruginosa is a suitable species representative of Dutch surface water circumstances, which ranks among the most problematic in water treatment. Its size, shape and cell surface characteristics make it an ideal surrogate for simulating undesired algae bloom conditions.
- The natural characteristic of algae to float suggests dissolved air flotation (DAF) could be an equally or more efficient particle (algae) removal technology when compared to sedimentation.

- The agglomeration (coagulation/flocculation) of particles (algae) is the main prerequisite for their efficient removal regardless of, but influenced by the down-stream solid-liquid separation process.

- Oxidants (ozone, KMnO₄) can significantly affect agglomeration (coagulation/flocculation) of algae and hence improve or deteriorate down-stream DAF removal efficiency (in terms of particles, turbidity, residual coagulant, etc.). The optimisation of this process is seasonally dependent driven by changes of species and their concentration.

- Apart from particle (algae) count, turbidity, residual coagulant, TOC/DOC, UV absorbance and other conventional analyses, the quantitative and especially qualitative characterisation of the effects in different process steps by computer image analysis will be a valuable tool for process kinetics assessment and modelling.

- Model water experimental research with laboratory cultured algae spiked into tap or reservoir water must be verified by pilot plant research using reservoir water and algae in their natural circumstances and environment.

### 2.4 Research methodology

Experimental work will be conducted on two levels:

1. At laboratory bench-scale, with model water, and using a DAF jar test experimental set-up (Fig. 2.1), and

![Scheme of the DAF jar test apparatus (6x1.8 L jars). S1 and S2: sampling points; C: coagulant; CA: coagulant aid; and pH: pH correction (by HCl or NaOH).](image)

Fig. 2.1
2. At pilot plant scale for experimental research with actual reservoir water of one location (Fig. 2.2).

Fig. 2.2 Scheme of the commercial mobile DAF pilot plant \( (Q_{\text{max}}=13 \text{ m}^3/\text{h}). \)

The model water research will be conducted by spiking semi-continuously, laboratory cultured \( M. \ aeruginosa \) to water originating from the Biesbosch reservoirs. Our ability to work with cyanobacteria in natural reservoir water is restricted due to their seasonal occurrence; this defines the period of the year for the pilot plant research from August to October.

The DAF jar test apparatus intended for the laboratory model water research is a standard apparatus equipped with DAF facilities. The pilot plant research is to be conducted with a commercial mobile DAF pilot plant unit with flexible coagulation and flocculation provisions. The research on ozone and KMnO\(_4\) application is also to take place at the two levels. For ozone production on both levels a Trailigaz LABO LO, France, ozone generator will be used.

The standard analytical methods that will be applied for the assessment of process efficiency comprise:

- Turbidity (Sigrist L-65, Switzerland),
- Residual coagulant (residual total Fe coagulant measured by atomic absorption spectrometry at 248.3 nm [NEN 6460]),
- Residual manganese (total and dissolved Mn measured by atomic absorption spectrometry at wavelength 279.5 nm for manganese [NEN 6466],
- TOC/DOC,
- UV absorbance at 254 nm, and
- Inverted microscope inspection (M40 Wild Leitz, Switzerland and Nikon Optiphot, Japan).
Measurements and analyses which are not commonly applied in practice, however offering an opportunity for improved process efficiency and kinetics assessment, are also to be applied:

- Particle (algae) count of particle >2.75 μm (HIAC-Royco PC-320, USA, flow-through, light beam scatter-based particle counter),
- Particle count of particles in the size range 0.3-5 μm (Particle Measuring Systems Inc./Liquid Batch Sampler LBS-100 and Microlaser Particle Spectrometer, Boulder, Co., USA),
- Electrophoretic mobility (Tom Lindström AB-Repair apparatus),
- O₃ concentration (iodimetric method),
- BrO₃⁻ concentration (ion-chromatography method),
- SEM - high resolution scanning electron microscopy,
- MFI - modified fouling index (KIWA standard measurements apparatus),
- Computer image analysis (Mini-Magiscan, IAS 25/IV25 Joyce-Loebl Ltd.).

The computer image analysis was used as one of the main tools for qualitative process kinetics assessment. This analytical technique is comprised of a microscope stage controller. It enables computerised registration, measurement and storage of a wide range of viewed object parameters such as its length, width, breadth, surface area, circularity, etc. The image analyses were performed on fresh samples, as well as on photographs of samples. For this purpose, a specially devised flat photo cell was connected at different locations of the jar test apparatus or the pilot plant unit, and samples were photographed or taken before and after flocculation, and after particle removal. Special care was taken to avoid disruption of flocculated material during the passage of the sample from the jar-test unit to the photo cell, by allowing low flow velocities adjusted through a system of valves. In case of DAF, the released air bubbles were also photographed and analysed. Professional high resolution black-and-white film AGFA 25 or Kodak TMAX 100 was used for the purpose, while forced development was applied for film processing. 30-100 fields, or more than 500 particles of each film shot were processed and analysed, using a ccd-camera (604*288 pixels) mounted to a Nikon Optiphot (Japan) microscope (at 40x magnification). The minimum detectable size under these circumstances was 1.9 μm. The software package Genias25 developed by Joyce-Loebl (UK) was used for data processing.

The computer image analysis results are presented in the form of particle size frequency and volume distributions. The frequency and volume distributions represent the number and the volume of recorded particle size range. For this purpose the recorded particles and/or floc material were approximated to spheres and presented in size ranges of 10 μm, from 0-200 μm. Particles >200 μm were also recorded (by image analysis and visually), however, they represented only a small percentage of the overall particle concentration which was effectively removed in treatment. The adopted size limit of 200 μm was found more relevant for the assessment of the overall DAF efficiency, since it included a more significant portion of the overall particle (floc) concentration, of size which is more problematic for DAF removal than the larger particles (flocs). The particle size of 50 μm, which is roughly the size limit of visually observable aggregates, was tentatively adopted as the size dividing the small from the large particle size range.

Statistical analysis of data was performed with the software package Statistica. One or two way analysis of variance (ANOVA), followed by multiple comparison and regression analysis among treatments were performed when appropriate. The same applies for the Mann-Whitney U-test.
Chapter 3

OPTIMISATION OF COAGULATION CONDITIONS FOR THE REMOVAL OF Microcystis aeruginosa BY DISSOLVED AIR FLOTATION OR SEDIMENTATION

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ABSTRACT: Analysis of surface water treatment practice in the Netherlands shows that cyanobacteria, especially *Microcystis aeruginosa* and *Oscillatoria agardhii*, are the main problem causing algae. Conventional (sedimentation) and advanced (dissolved air flotation) treatment of algae laden (model) water were studied. The agglomeration (coagulation/flocculation) phase was found to determine the process efficiency and hence to be the prerequisite for process improvement. Both processes were assessed in terms of their removal efficiency for the cyanobacterium *M. aeruginosa*. Relevant process parameters were studied, including the influence of coagulant (FeCl₃) dose, coagulation pH, flocculation time, energy input (G value), single-stage versus tapered flocculation, application of a cationic polyelectrolyte (Superfloc C-573) as coagulant aid, and surface loading. The process efficiency was assessed as a function of the agglomeration and the resultant particle (floc) size distributions. The results were evaluated in function of highlighting the occurring process mechanisms.

3.1 INTRODUCTION

The new interest in surface water treatment in the Netherlands has called for study of the specific problems caused by algae. An investigation carried out at five drinking water production plants in the Netherlands utilising surface water (relating to 60% of the total Dutch drinking water production from surface water), showed that the main problem causing algae are the cyanobacteria, in particular *Microcystis aeruginosa* and *Oscillatoria agardhii* [1] (Chapter 1). Their seasonal blooms impose short- and long-term treatment modifications with significant additional costs. Apart from developing water quality management measures, the understanding of efficient treatment technologies needs to be expanded.

In treatment, the agglomeration, i.e. coagulation/flocculation phase is likely the most critical. It can be influenced by conditioning of the algae (application of a chemical oxidant), and/or physical conditioning of the water (microstraining), as well as by optimising the subsequent solid-liquid separation process [2, 3, 4]. In practice, for the latter conventional (sedimentation) and more advanced (dissolved air flotation [DAF]) processes are used, followed by final filtration. It has been recommended to evaluate the flotation-filtration and sedimentation-filtration treatment options as integrated processes [5]. By consequence this pertains equally to the agglomeration (coagulation/flocculation) step [6].

The low density of algae (0.99-1.2 g/cm³) and their phototactic/phobic and chemotactic/phobic responses tend to keep them in a continuously floating state. Optimised coagulation with respect to coagulant dose and pH is required both for DAF and sedimentation in order to destabilise the algae. The stability of algae in suspension is ascribed to the repulsive electrostatic interactions caused by surface charges that are negative for pH 2.5 - 11.5 [7], and to steric effects of water bound to cell surface and of adsorbed macromolecules or EOM [8]. DAF without the use of coagulants has been found to be inefficient [5, 9]; apart from the mentioned steric hindrance, the slightly negative surface charge of air bubbles contributes to this [10, 11]. Thus, as in DAF particle destabilisation is more important than large floc size [12], coagulation conditions that produce flocs or particles of little or no charge are required.
According to classical coagulation theory [6] efficient particle destabilisation and high process efficiency is to be expected at pH below the iso-electric point (IEP=6-7 for iron hydroxy complexes), however, other reports have suggested that optimal algal removal (in direct filtration) occurred at pH of 8-8.8 [2]. This, however, does not necessarily imply that more efficient coagulation takes place at the higher pH. Namely, in case of direct filtration the time interval between coagulant addition and the filtration step is relatively short (in the range of a few minutes), suggesting that higher pH (>7.5) is needed in order to assure faster and complete coagulant (iron) hydrolysis. Thus, the formation of difficult to remove, colloidal iron-organic complexes is partially avoided. Furthermore, in cases of higher Ca\(^{2+}\) concentrations, preferential complexation of Ca over Fe with organic matter occurs at pH > 8. Both factors render more coagulant available for more efficient destabilisation of colloidal and particulate matter present, including algae. In the same study [2] the application of cationic polyelectrolyte enhanced process efficiency and reduced coagulant dose. Other experiences with the use of polyelectrolytes as coagulant aids in the context of DAF were controversial with respect to obtained benefits [5, 13].

Furthermore, small (10-30 \(\mu\text{m}\)) and light flocs should be produced by the coagulation/flocculation process [10]. Due to the inverse relation between flocculation mixing intensity and time on one hand, and floc size on the other [14], flocculation G values of 30-80 \(\text{s}^{-1}\) have been proposed, while flocculation times as short as 5 to 6 minutes were found to suffice [4, 5]. With respect to DAF, one can assume that the rising air bubbles act as a rising filter bed which collects particles on its way to the water surface, in analogy to the DAF kinetic model proposed by Malley and Edzwald [12]. In this context, it seems feasible to investigate the possible existence of an optimum flocculation Gt range for DAF (optimum direct filtration conditions occur within a flocculation Gt range of 15,000-40,000 [15]). On the other hand, coagulation conditions that produce flocs with good settling characteristics are essential for efficient sedimentation. The settling characteristics of a flocculent suspension depend on floc size, floc density, water temperature [16] and in some cases initial particle number concentration [17]. Good settling is generally achieved at high(er) coagulant doses, low flocculation energy input (G=10-40 \(\text{s}^{-1}\)) and long(er) flocculation times (30-60 min). Although tapered flocculation seems more appropriate for sedimentation (providing longer flocculation times and favourable floc structure due to diminishing energy input) it is also applied in DAF, as in the case of the DZH (Dune Water Supply Company South Holland) and EWR (Energy and Water Supply Company Rhineland) treatment plants.

Malley and Edzwald [18], comparing sedimentation and DAF performance on laboratory scale in terms of particle removal, showed that as temperature decreases, the performance of DAF over that of sedimentation increases. They also found comparable performance with flocculation periods of 5 minutes for DAF, and of 20 minutes for sedimentation. These findings were based on experiments with model water prepared by spiking water with aquatic fulvic acid and montmorillonite clay, as well as with natural water. Compared to earlier research, the removal efficiencies are modest, especially in the case of DAF. Janssens [5] reported 65 - 92 % removal of naturally occurring cyanobacteria including \(M.\) \(aeruginosa\) by DAF, but lower efficiency was observed for other algae including the cyanobacterium \(M.\) \(pulvera\) (small size of 2-3.4 \(\mu\text{m}\) and without gas vacuoles); it was not mentioned whether the higher removal efficiency was achieved when coagulant aid, which might have enhanced
the efficiency of the tested alum, PACI (polyaluminium chloride) and ferric chloride coagulants. Edzwald and Wingler [19] reported a DAF removal efficiency of 96.8 and 99.8% for laboratory cultured Chlorella (Chlorophyceae) and Cyclotella (Bacillariophyceae) respectively, spiked into natural reservoir water; the initial concentrations used in these experiments were 10 and 5 times higher than in our experiments, while alum and PACI (polyaluminium chloride) were tested as coagulants at a low pH of 6.5 for the first and 5.5 for the second. The high algae concentration asserted a positive impact on the coagulation/flocculation and DAF efficiency. Furthermore, the low coagulation pH conditions are not representative for treatment practice and result in adsorption coagulation, which may have positively affected the efficiency. Zabel [20] found that similar initial concentrations of M. aeruginosa \(10^5\) cells/mL resulted in 98% removal in full-scale DAF operation, while under the same conditions upflow floc blanket sedimentation efficiency was 76%. These results were achieved by using aluminum sulfate as coagulant at a relatively low pH of 6.5-7.2. In the case of chlorinated ferrous sulfate coagulant at pH of 8.3-8.7, the removal efficiencies (of other algae species) were lower; worst results were obtained for Stephanodiscus: 40% by sedimentation and 83% by DAF.

These and other data from literature and practice strongly suggest that the removal efficiency of algae varies for both processes, depending on raw water characteristics, alga species, their morphology and physiology, and treatment process parameters, notably coagulation pH, type and dose of coagulant, flocculation energy input and time and process loading rates. In treatment, it can be surmised that the algal removal efficiency relies most significantly on good particle agglomeration (coagulation and flocculation). Therefore, when working with laboratory cultured algae, the potential interference of the complexing agents used in the preparation of the algae growth medium on the coagulation/flocculation step (binding of coagulant making it inaccessible for floc growth) must be taken into account [21]. Furthermore, the occasional particle count of acidified effluent samples showed that a substantial part (15-20% for the higher coagulant doses) of the particle count can be attributed to particulate residual coagulant. The definition of particle removal efficiency and the comparison of results among different studies, become even more complicated.

In this chapter the optimisation of the agglomeration phase for both alternative processes is discussed and assessed. Model water experiments were used for determining removal efficiency for M. aeruginosa. The efficiency of the two processes is compared in the context of cost-effective M. aeruginosa removal, while the results are evaluated in the light of existing theoretical and operational knowledge related to the two processes. Relevant process parameters were studied: coagulant \(\text{FeCl}_3\) dose, pH, flocculation time and energy input (G value), single stage versus tapered flocculation, application of cationic polyelectrolyte (Superfloc C-573) as coagulant aid, and surface loading. This is done in order to clarify some of the inconsistencies met in literature and practice, e.g. the applicability of very short flocculation times for DAF, the effect of tapered versus single stage flocculation, determination of the optimal energy input (G value), the impact of polyelectrolytes on DAF efficiency, etc. The underlying process mechanisms and kinetic aspects are also discussed, while a broader discussion on the mechanistic theory of DAF is given in Chapter 7.
3.2 EXPERIMENTAL PROCEDURES

3.2.1 Experimental design

The experimental set-up consisted of a modified KIWA - standard jar test apparatus with incorporated DAF facilities that could be connected to small-scale filters (diameter 60 mm, height 400 mm) with sand as filtration medium (commercial fraction 0.80-1.25 mm, bed thickness 200 mm) (Fig. 3.1). Initially, both sedimentation and DAF were optimised without considering further treatment by rapid filtration; at a later stage (specifically mentioned in Results and Discussion) rapid filtration was also included at a constant filtration rate of 10 m/h, similar to the five full scale filtration installations studied. The filtration itself was not optimised due to time constraints and it was applied in a limited number of experiments in combination with previously optimised up-stream DAF and sedimentation conditions.

Fig. 3.1 The modified jar test apparatus with DAF facilities, including a small scale filter unit.

For both, DAF and sedimentation, the experimental procedure included coagulation at a G value of 1,000 s⁻¹ for 30 s, temperature of 20°C at a pH of 8, while the flocculation G (Gₚ=10, 30, 50, 70, 100 and 120 s⁻¹) and flocculation time (tₚ=5, 10, 15, 25, 30 and 35 min) were varied in a range which aimed at including low, medium and high values respectively. The adopted G values were converted into the appropriate number of revolutions of the stainless steel flocculation paddle (b×h=7.5x2.5 cm) by using a previously established calibration line (log-log scale). Three-stage tapered flocculation for DAF was tested at diminishing energy input (G₁= 82, 49, 23 s⁻¹) and equal flocculation time (t =3x8 min), same as in the Scheveningen DAF plant of DZH. The tested coagulant (FeCl₃·6H₂O) doses were in the range of 0 - 15 mg Fe(III)/L. The cationic polyelectrolyte Superfloc C-573 was used as a coagulant aid in the range of 0 - 1.5 mg C-573/L for DAF and 0 - 3 mg C-573/L for sedimentation, combined with the previously optimised Fe coagulant dose. The polyelectrolyte dose range choice was based on providing roughly 1/10th of the determined optimal coagulant dose. The
sedimentation time range covered the low, medium and high range of values \( t_s = 10, 20, 30, 45, 60 \) and 90 min), while for DAF typical recirculation ratios \( (R=5, 8 \) and 10\%) and saturator pressures \( (P=500, 600 \) and 700 kPa) were tested \([10]\). After releasing the recycled flow into the jar test unit, slow mixing at a \( G<10 \) s\(^{-1}\) was applied for 30 s, followed by a period of 4 min flotation (without any mixing), after which sampling took place.

3.2.2 Algal suspension

The investigated cyanobacterium were semi-continuously laboratory cultured, single cells of *M. aeruginosa*. The algae were provided from two sources: the Microbiology Laboratory, University of Amsterdam, the Netherlands, and the Institute of Freshwater Ecology, Windermere Laboratory, United Kingdom. The algae were cultured on Jaworski growth medium in 5 L vessels, at 20 °C and 1,000 lux light intensity, according to directives and recipes \([22]\) (Appendix 3.1). The algae were spiked into water originating from Biesbosch storage reservoirs. This reservoir system supplies water to the city of Rotterdam, partly to the city of Dordrecht, the provinces of South-West Netherlands and North-West Brabant. The water is originally eutrophic river Meuse water, but efficient water quality management during the six months of impoundment results in the production of almost oligotrophic conditions with generally low algae counts and average chlorophyll concentrations of \( 5.6 \) µg/L \([23]\). The initial algal concentration in our model water was standardised by particle (algae) count (HIA) as \( = 10,000 \) cells/mL. The rationale behind this standardisation was to simulate an algae concentration which is considered problematic and representative for water treatment. This concentration roughly corresponds to the average monthly cyanobacteria concentration in one of the most seriously algae affected water resources, namely the WRK III water treatment plant reservoir (Fig. 1.4). Colonies of *M. aeruginosa* are the prevalent cyanobacterium species during such blooming episodes. The colonial form of this species is relatively easily removed by e.g. the initial WRK III microstraining, while the single cell form which is a product of natural disintegration of colonies (by the end of their life cycle), or mechanically induced disintegration due to e.g. high shear related to the initial pumping stage, regularly penetrates treatment and is encountered in treatment plant effluents \([1]\). Thus, the simulated situation is even more serious and difficult with respect to treatment, since we are dealing with the same concentration of the single cells form of *M. aeruginosa*.

Providing algae continuously at constant and comparable quality from the culture was a difficult task. Spiking identical volumes of algae suspension from the two algae cultures resulted in the desired particle (algae) count, however, the corresponding turbidity varied from 1.5 to 2.5 FTU in the case of the Amsterdam algae and from 3 to 4.1 FTU in the case of the Windermere algae. In both cases the spiked algae were in the stationary growth phase which was reached approximately 14 days after the culture start-up. Prior to spiking, the appropriate volume of algae culture was strained through a 35 µm mesh, in order to discard large lumps - agglomerates of algae debris and cellular organic matter, which was increasingly formed at later growth stages of the cultured algae. Thus, a simulation of the single cell form of *M. aeruginosa* was accomplished. The model water temperature was kept constant at 20°C in order to simulate conditions during late summer and early autumn blooms.
3.2.3 Analysis methods

In the context of providing efficient down-stream filtration and longer filter runs the performance goal for sedimentation and DAF was set for turbidity <1 FTU, residual coagulant <1 mg Fe/L, and minimal particle (algae) count (HIAC); DOC removal was to be quantified.

Previous investigations [2] have shown that the use of turbidity as a lumped parameter for the evaluation of process efficiency is often inadequate, especially in the lower turbidity range (<0.5 FTU), e.g. in the case of filtration product water. Namely, the low filtrate turbidity generally cannot be correlated with the accompanying low particle count. Particle count measurements are essential in such cases in order to better identify the mechanisms and phenomena underlying coagulation conditions. Thus, process efficiency evaluation was based on measurements of turbidity (Sigrist L-65, Switzerland) and particle (algae) count measurements (HIAC-Royco PC-320, USA), while inverted microscope count (M40-Wild Leitz, Switzerland) and computer image analysis were performed periodically. Residual coagulant as Fe<sub>total</sub>, DOC and electrophoretic mobility (EM) (Tom Lindstrom AB-Repair) were also measured. The sampling locations are given in Fig. 2.1 (Chapter 2). Samples were taken for raw water and after full treatment, except for EM, inverted microscope analysis, and computer image analysis, when additional samples of flocculated water were analysed. Flocculated water samples contain algae and Fe hydrous oxides flocs. A standard sample volume of 0.5 L was abstracted after DAF from the taps at the bottom of all the jars simultaneously, within a standardised time of one minute. For sedimentation the same procedure was performed, using a vacuum pipe system which abstracted water from the upper half of the jars simultaneously. In both cases attention was paid not to disturb the floated/settled matter which would affect the measurements. Glass bottles were used for sampling. Most measurements were conducted on spot, except for Fe<sub>total</sub> and DOC. These were done on preserved samples kept at a temperature of 4 °C, with one-two days delay. Fe samples were preserved in plastic bottles by adding 0.5 M HCl to reach a pH <2 and dissolve all iron present. DOC samples were kept in glass bottles to avoid the impact of plastic on measurements.

To ensure reproducibility of the experimental results, the performance of the jar test apparatus was periodically (weekly) tested under identical experimental conditions in all six jars. The results which are further discussed are representative of multiple experimental analysis. The impact of variations of initial experimental conditions on the results, i.e. initial algae count and turbidity was also considered and statistically analysed. Statistical analysis of data was performed with the Statistica software package. Two way ANOVAs followed by multiple comparison among treatments were performed when appropriate. The same applies for the Mann-Whitney U-Test.

The computer image analysis was performed with a Mini-Magiscan (IAS 25/IV25 Joyce-Loebl Ltd., UK) image analysis system (Fig.3.2), producing information about particle size frequency and particle volume distributions.
These analyses were performed on fresh samples, as well as on photographed samples using previous experience from a similar research [24]. For the purpose of the latter, a specially devised flat photo cell was connected to the jar test apparatus. Representative samples of raw, flocculated, and treated (DAF, sedimentation and filtration) water were passed through the photo cell and photographed. The same applies for (algae free) water into which the DAF recycled stream was introduced and released air bubbles were photographed. Professional high resolution black-and-white film AGFA 25 or Kodak TMAX 100 was used, while forced development was applied for film processing. Hundred fields of each picture were processed and analysed, using a ccd-camera (604*288 pixels) mounted to a Nikon Optiphot microscope (at 40x magnification). For verifying the representativity of the samples, multiple shots of the same sample were analysed occasionally. The software package Genias25 developed by Joyce-Loebl Ltd., (UK) was used for data processing.

Results from computer image analysis are presented in the form of particle size frequency or volume distributions. These depict the recorded frequency (absolute or relative percentual value) or volume of suspended material (detection limit of 1.9 μm), in a particular particle size range, after different treatment steps. For this purpose the recorded particles (flocs) material were approximated to spheres. For verifying the reproducibility of the applied analytical technique, multiple shots of the same sample were analysed regularly. Particle size distributions departed strongly from normality. Particle size frequency distributions from different sets of experiments performed under identical conditions were compared by the application of the chi-square test. Testing the hypothesis that the obtained particle size distributions were identical, resulted in a probability level of P=0.999, suggesting well comparable particle size distributions and good results reproducibility.
3.3 RESULTS AND DISCUSSION

3.3.1 Turbidity and particle (algal) count

For turbidity in the range of our interest (with sedimentation and DAF effluent turbidity mostly >0.5 FTU) we found a linear correlation between turbidity and particle count \( (r^2=0.99) \) for each of the cultured algae strains, however, the regression lines had different slopes (Fig. 3.3).

This suggests different morphology of the two strains. Particle count/turbidity ratio differences were also observed with different algae growth stages, as well as under slight changes of growth conditions, e.g. light intensity. The phenomenon of different algae morphology features of the same species under different growth conditions has been noted in nature also, e.g. in the case of the diatom *Stephanodiscus hantzschii*, a species known to develop bristle like appendages in autumn and winter, which hampers its removal [21].

![Graph showing particle count versus turbidity for tap water spiked with cultured *M. aeruginosa.*](image)

3.3.2 Optimisation of agglomeration

a. Coagulation pH

At pH 8 organic particle agglomeration is likely to be solely achieved through sweep coagulation because of the higher solubility of the metal hydrolysate and the dominance of negative metal hydroxide compounds [25]; here this was confirmed by the negative surface charge of all floc material, also under conditions of optimal removal. Figs. 3.4 and 3.5 describe particle size frequency distributions after flocculation and after DAF at pH 6 and pH 8. After flocculation, a more pronounced reduction of the smaller size particles \( (<50 \mu m)\),
and a larger share of formation of larger size particles (> 50 μm) frequency were observed at pH 6 as compared to pH 8.

Fig. 3.4 pH 6, 10 mg Fe(III)/L, particle size frequency distribution before and after DAF. Experimental conditions: R=5%, P=500 kPa.

Fig. 3.5 pH 8, 10 mg Fe(III)/L, particle size frequency distribution before and after DAF. Experimental conditions: R=5%, P=500 kPa.

In both cases the applied coagulant dose produced flocs larger than 50 μm which were efficiently removed. However, it is evident that at the lower pH conditions adsorption coagulation and charge neutralisation substantially contributed to the flocculation beside the simultaneously occurring and dominant sweep coagulation which is coagulant dose dependent.
This resulted in more efficient flocculation and almost doubled particle removal efficiency at the lower pH, suggesting that adsorption coagulation plays an important role in algal flocculation. Electrophoretic mobility measurements confirmed that algae charge neutralisation occurred under these conditions, which is also in accordance with findings of Bernhardt and Clasen [6, 26]. However, the practical implications of these findings are mostly indicative. Namely, pH control for the sole purpose of coagulation enhancement is in practice not always feasible. The application of polyelectrolytes, in this case preferably cationic, could be a suitable alternative to achieve particle charge neutralisation.

b. Flocculation conditions

Results here confirmed that DAF required considerably shorter flocculation times than sedimentation (tₚ=10 compared to 30 minutes), however, a lower flocculation G value of 10 s⁻¹ performed equally well or better in DAF than higher G values. The same low G value was applied by Edzwald and co-workers resulting in better particle removal by DAF compared to sedimentation [8], and in excellent algae removal [19].

Here, results did not allow determination of an optimal Gt region for DAF. This was due to the fact that a flocculation G value of 10 s⁻¹ and of 70 s⁻¹ consistently resulted in similar removal efficiencies, better than the other tested G values, thus suggesting other specific factors that influence DAF efficiency. Similar to what Janssens [5] reported, tapered flocculation which is generally considered favourable for sedimentation did not significantly affect DAF efficiency.

Beside chemical factors, floc size played an important role in process efficiency in both, sedimentation and DAF. Image size analyses showed an inverse relation between flocculation energy input (G value) and floc size (see also Chapter 6). A low G value of 10 s⁻¹ produced a floc volume distribution which led to the highest DAF removal efficiency (Fig. 3.6), as verified by (HIAC) particle count, turbidity and residual Fe measurements. Comparison of the particle (floc) volume distributions after flocculation at G=10 s⁻¹ (Fig. 3.6) and G=23 s⁻¹ (Fig. 3.7), suggests that the increase of energy input resulted in denser floc structures (see also Chapter 6).

DAF efficiently removed the particles in the larger particle size region (>50 μm) both at G=10 (Fig. 3.6) and 70 s⁻¹ (data not presented). Therefore, the common recommendation that DAF requires high G values in order to produce small (10-30 μm), strong, shear resistant flocs, is not supported by these results. Sedimentation on the other hand, was found to be favoured here with floc size distributions obtained by G values of 10-30 s⁻¹, yielding slightly better results at G=30 s⁻¹ (data not presented). A Mann-Whitney U-Test, for this G value, testing significant differences in efficiency between flocculation times tₚ of 20 and 30 min, showed no significant differences for particle (algae) count, but significant differences for turbidity. The initial (particle count and turbidity) conditions for the analysed sets of experiments did not differ significantly suggesting that the results can be reliably compared. Finally, it is suggested that the floc size/density ratio plays an important role in the DAF and sedimentation processes. This aspect will be discussed in more details in Chapter 6.
Fig. 3.6  \( G=10 \text{ s}^{-1} \), particle volume distribution before and after DAF. Experimental conditions: 3 mg Fe(III)/L, \( G_t=10 \text{ s}^{-1} \), \( t_t=8 \text{ min} \), R = 8\%, \( P = 600 \text{ kPa} \).

Fig. 3.7  \( G=23 \text{ s}^{-1} \), particle volume distribution before and after DAF. Experimental conditions : 3 mg Fe(III)/L, \( G_t=23 \text{ s}^{-1} \), \( t_t=8 \text{ min} \), R = 8\%, \( P = 600 \text{ kPa} \).

In case of sedimentation, kinetics suggests that under the conditions of the study efficient sedimentation requires an increase in initial particle concentration through the application of higher coagulant dosages than those required for DAF. Low G values are expected to promote formation of floc size volume distributions with a higher frequency in the larger particle size range, as well as flocs with lower density. The low G values also produced floc size distributions favouring DAF, of which the performance is not solely dependent on large floc
sizes. Mean floc and bubble size dimensions calculated by image analysis enabled calculation of the coefficient of particle-bubble attachment efficiency \( \alpha_{pb} \) [8, 28], which will be discussed in more detail in Chapter 7.

c. Polyelectrolyte as coagulant aid

The high DAF efficiency achieved at pH below the iso-electric point (IEP) for iron hydroxocomplexes (IEP=6-7) (see earlier), emphasizes the role of adsorption-coagulation and charge neutralisation for particle removal. This suggests potential process efficiency benefits in case of applying cationic polyelectrolytes as coagulant aids.

Investigations here showed that low cationic polyelectrolyte (Superfloc C-573) doses of 0.5 and 1.0 mg C-573/L, in combination with the previously established optimal primary coagulant doses (3 mg Fe(III)/L for DAF and 10 mg Fe(III)/L for sedimentation), significantly raised particle (algae) removal efficiency: for DAF up to 94.5% and for sedimentation up to 98.9%. This was accompanied by charge neutralisation of the algae at a coagulant aid dose somewhat higher than the established optimum, as verified by electrophoretic mobility measurement. Particle volume distributions of flocculated water with and without the addition of coagulant aid (Fig. 3.8) showed a distinct difference: a clear improvement was observed in agglomeration performance in the case with polyelectrolyte addition, expressed in a more pronounced larger particle size (> 50 \( \mu \)m) contribution.

![Graph](image.png)

Fig. 3.8 10 mg Fe(III)/L and Superfloc C-573 as coagulant aid, particle volume distribution of flocculated water with and without polyelectrolyte. Experimental conditions: pH 8, \( G_i = 30 \text{ s}^{-1}, t_i = 30 \text{ min} \).

Although the floc volume distribution for the case of 0.5 mg Superfloc C-573 was more pronounced in the large particle size range compared to that for 1.0 mg Superfloc C-573/L, the latter produced better results after sedimentation. It is suggested that the better sedimentation efficiency is related to a denser floc structure resulting from the higher
polyelectrolyte dose. The smaller, 0.5 mg Superfloc C-573/L dose, favoured efficient DAF, which improved the algae flocculation and resulted in bigger and lighter floc material than was produced by the 1.0 mg C-573/L dose.

Though the filtration was not included in this particular set of experiments, it can be that the low DAF and sedimentation effluent algae concentration would enable longer and more economical filter operation. This may possibly be disturbed to a limited extent by the residual polyelectrolyte which may account for filter blockage and filter backwash problems.

3.3.3 Sedimentation versus DAF

The goals effluent turbidity (<1 FTU) and residual coagulant (<1 mg Fe/L) were achieved by both processes. The DOC removal was around 25%, relying on coagulation efficiency, but not on the solid-liquid separation process, as was also reported by Malley and Edzwald [18]. However, in the case of initial model water turbidity of 3-3.5 FTU (Windermere algae), the 1 FTU turbidity goal was achieved only when cationic polyelectrolyte was used as coagulant aid, or when longer and not very feasible flocculation times were applied (>30 min). Figs. 3.9 and 3.10 show that in order to attain maximum particle (algae) removal efficiency, sedimentation required approximately three times higher coagulant dose (10 mg Fe(III)/L vs. 3 mg Fe(III)/L).

![Graph showing removal efficiency](image)

**Fig. 3.9** Removal efficiency after sedimentation (SED) and after sedimentation-filtration. Initial conditions: see Section 3.2. Experimental conditions: pH 8, $G_r=30$ s$^{-1}$, $t_f=30$ min, $t_s=60$ min, $v=10$ m/h.

Consequently, the sedimentation process would also result in higher sludge production, that in addition has worse dewatering characteristics [20]. Similarly, the sedimentation alternative required a three times longer flocculation time ($t_f=30$ min vs. 10 min) and higher flocculation
energy input \( (G_r=30 \text{ s}^{-1} \text{ vs. } 10 \text{ s}^{-1}) \), as well as a significantly lower process loading rate \( (t_r=60 \text{ min vs. } \text{standardly applied } 10-30 \text{ min}) \) in order to achieve optimal process efficiency. The flocculation \( G \) values of 10 \( \text{ s}^{-1} \) and 70 \( \text{ s}^{-1} \) (the latter being in the range generally considered as favourable for DAF) consistently resulted in similar DAF efficiency.

![Graph showing removal efficiency](image)

**Fig. 3.10** Removal efficiency after DAF, and after DAF-filtration. Initial conditions: see Section 3.2. Experimental conditions: \( \text{pH } 8, G_r=70 \text{ s}^{-1}, t_r=10 \text{ min, } R=8\%, P=600 \text{ kPa, } v=10 \text{ m/h.} \)

The coagulant doses for which maximum particle and turbidity removal was achieved in the DAF and the sedimentation were 3 and 10 mg Fe(III)/L, respectively. Although the residual coagulant concentration was higher for higher coagulant doses, the percentual coagulant removal efficiency after DAF and after sedimentation generally increased with the coagulant dose. The respective residual coagulant concentration carried over from DAF or sedimentation to the filtration step was 0.1-1.5 mg Fe/L, and thus lower than dosages commonly applied in direct filtration.

Figs. 3.11 and 3.12 represent particle volume distributions created by coagulant doses of 6 and 15 mg Fe(III)/L. Flocculation with 6 mg Fe(III)/L resulted in flocs of 10-50 \( \mu \text{m} \) and 50-100 \( \mu \text{m} \), while the 15 mg Fe(III)/L dose resulted in larger amounts of flocs in both sizes. The particle volume distribution after the sedimentation step shows that the two coagulant doses resulted in a relatively similar floc size carried over to the filtration, however, a better filtration efficiency was observed for the 15 mg Fe(III)/L dose, as determined by particle distribution measurements and also corroborated by HIAC particle count. This can be ascribed to the higher residual iron concentration after the sedimentation at this coagulant dose, and hence an enhanced "direct" filtration effect. The model water in these experiments was relatively free of organic matter (TOC=2.5 mg C/L) which otherwise might have complexed significant quantities of the hydrolysed iron coagulant species and render it unavailable for the direct filtration effect.
Fig. 3.11 Sedimentation-filtration, 6 mg Fe(III)/L, particle size volume distribution. Initial conditions: see Section 3.2. Experimental conditions: pH 8, Gt=30 s⁻¹, t_r=30 min, t_s=60 min, v=10 m/h.

Fig. 3.12 Sedimentation-filtration, 15 mg Fe(III)/L, particle size volume distributions. Initial conditions: see Section 3.2. Experimental conditions: pH 8, G_t=30 s⁻¹, t_r=30 min, t_s=60 min, v=10 m/h.

These results may be considered only as qualitative as the small diameter of the filters may cause wall effects; similarly, the absence of filter ripening (due to the small water quantities filtered), may lead to underestimation of the filters performance and efficiency.

From the point of view of final product water quality - treatment plant effluent, the achieved algae removal efficiency by both treatment processes is to be considered inadequate. At
optimal conditions in this study, sedimentation performed somewhat better than DAF in terms of algal removal efficiency (maximum removal of 87% for sedimentation versus 71% for DAF). Achieving more than 99% removal efficiency in our study would suggest a residual of <100 cells/mL, a concentration which was often close to the demineralised water particle count. Although no standards exist for algae in drinking water, a residual algae concentration of 100 - 500 cells/mL (achieved by DAF and sedimentation under optimal process conditions with the use of cationic polyelectrolyte as coagulant aid) is relatively high. The down-stream filtration is the final barrier to retain colloidal and particulate matter.

Optimisation of the filtration step is expected to further raise the particle removal efficiency from 94.7% (sedimentation-filtration) and 90% (DAF-filtration). The generally higher recorded removal efficiency of the filtration following the sedimentation (Fig. 3.9 and 3.10), is attributed to the larger size of the residual floc material after sedimentation. This is the consequence of the lower flocculation G value of 30 s⁻¹ as compared to the 70 s⁻¹ applied in the DAF-filtration. The fact that removal efficiency is critically dependent on coagulant dose in the sedimentation-filtration case (Fig. 3.9) also suggests that it is the upper filter layer that has functioned in filtration, as reported also elsewhere [28]. On the other hand, the slightly steeper slope of the efficiency versus coagulant dose line in the case of DAF-filtration (Fig. 3.10), suggests that apart from the flocculation G value and concomitant floc size, other factors influenced the filtration efficiency.

3.3.4 Statistical analysis

A Mann-Whitney U-Test comparing the particular combinations of optimal DAF and sedimentation conditions (Fig. 3.13) resulted in insignificantly different particle removal efficiency (P=0.087) and significantly different turbidity removal efficiency (P=0.017).

![Box plot](image)

**Fig 3.13** Particle (algae) and turbidity removal efficiency for optimised DAF and sedimentation (SED). Number of data sets analysed n=10. Notation: Fe(III)-coagulant dose; G-flocculation energy input; t-flocculation time; R/P-recirculation ratio/saturator pressure; t_{sed}-sedimentation time.
A Mann-Whitney U-Test comparing DAF \((G_f = 10 \text{ s}^{-1})\) and sedimentation \((G_f = 30 \text{ s}^{-1})\) on a broader scale (different flocculation time values being pooled within each of these two treatments) yielded no significant differences both, for particle (algae) and turbidity removal efficiency \((P > 0.05)\). The flocculation G values of 10 and 70 \text{ s}^{-1} were tested by two way ANOVA for a flocculation time of 10 and 20 minutes (Fig. 3.14), and are presented in the Table 3.1.

![Box plot of particle count and turbidity removal efficiency](image)

**Fig. 3.14** Two way ANOVA of DAF particle (algae) and turbidity removal efficiency for different flocculation G and t values (R-recirculation ratio, P-saturator pressure). Number of analysed data sets \(n = 24\).

**Table 3.1** Results from the ANOVA, quantifying the degree of correlation between flocculation energy input (G) and time \((t_f)\), and their effect on particle and turbidity removal efficiency \((n = 24)\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Turbidity</th>
<th>Particle count</th>
</tr>
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<tbody>
<tr>
<td>Factor</td>
<td>(P)</td>
<td>(P)</td>
</tr>
<tr>
<td>(G)</td>
<td>0.66</td>
<td>N.S.</td>
</tr>
<tr>
<td>(t_f)</td>
<td>0.087</td>
<td>N.S.</td>
</tr>
<tr>
<td>(G \times t_f)</td>
<td>0.049</td>
<td>*</td>
</tr>
</tbody>
</table>

\(P\): significance level  
N.S.: not significant  
*: significant \((P < 0.05)\)

It can be concluded that the effects of \(G\) and \(t_f\) on the particle and turbidity removal efficiency, independent of each other, were not significant. The only significant effect on efficiency was asserted through the interaction of the flocculation \(G\) and \(t_f\). This implies that for the lower flocculation \(G\) value increase of \(t_f\) increases the efficiency and for a higher flocculation \(G\) value increase of \(t_f\) decreases the efficiency.
Multiple comparison between different \( t_r \) within each \( G \) value, and between different \( G \) within each \( t_r \) (CER=0.05, EER=0.013) shows that the only significant difference exists between DAF at \( G=10 \ \text{s}^{-1} \) and \( t_r=20 \ \text{min} \), and \( G=70 \ \text{s}^{-1} \) and \( t_r=20 \ \text{min} \). Table 3.2 sums up the results of the multiple comparison analysis.

Table 3.2  Multiple comparison test between different treatment (varied \( G \) and \( t_r \)) and the effect on particle and turbidity removal efficiency (\( n=24 \)).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Particle count</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G=10 \ \text{s}^{-1}, t_r=10 \ \text{min} )</td>
<td>ab</td>
<td>a</td>
</tr>
<tr>
<td>( G=10 \ \text{s}^{-1}, t_r=20 \ \text{min} )</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>( G=70 \ \text{s}^{-1}, t_r=10 \ \text{min} )</td>
<td>ab</td>
<td>ab</td>
</tr>
<tr>
<td>( G=70 \ \text{s}^{-1}, t_r=20 \ \text{min} )</td>
<td>a</td>
<td>ab</td>
</tr>
</tbody>
</table>

Note: a, b and ab represent similarities between removal efficiency under different treatment conditions.

The ANOVA of the initial particle count for the four sets of experimental conditions showed that the initial particle count didn’t vary significantly, suggesting that the particle removal results could be compared. Initial turbidity, however, differed significantly for different \( t_r \), which may have affected the results from the experiments and made the above observations not fully correct. This implies that the results obtained from this set of experiments can not lead to fully reliable conclusions. Similar results were obtained if the initial particle (algae) count and turbidity were introduced as covariates in the ANOVA.

3.4 CONCLUSIONS

A correlation was found between particle count and turbidity (\( r^2=0.99 \)), however of different slopes for the two different algal strains. Consequently, turbidity may be a useful parameter for proses efficiency assessment, however less accurate than particle count.

Highest particle and turbidity removal was obtained at pH below the iso-electrical point (pH 6), related to particle (algae) charge neutralisation phenomena, and improved flocculation. The coagulation pH had a pronounced effect on the particle size distribution after flocculation; the concentration of smaller particles (\(<50 \ \mu m\)) was more significantly reduced on account of the formation of a a more significant concentration of larger particles (\(>50 \ \mu m\)) at pH 6 versus pH 8. Furthermore, the algae charge neutralisation which occurred at coagulation pH 6 contributed to the increased DAF efficiency due to improved particle (floc)-bubble attachment, the air bubbles being negatively charged.

Tapered flocculation did not improve DAF efficiency, while the possible existence of an unambiguous optimal Gt range for DAF, although suggested by statistical analysis, could not be confirmed. Sedimentation required an increase of initial particle concentration through the addition of high coagulant dosages in the range of 10 mg Fe(III)/L, and low flocculation G values in the range of 10-30 s\(^{-1}\). This resulted in floc volume distributions with high frequency
both in the smaller (<50 μm) and larger (>50 μm) particle size ranges. A low flocculation G value of 10 s^{-1} resulted in similar and better algae removal efficiency by DAF than the value of G=70 s^{-1}, producing a floc size distribution with larger and lighter flocs, favouring efficient DAF. The interaction between the flocculation G and t values was found as the only significant factor affecting the DAF process efficiency, each of them separately having no statistically significant effects on removal efficiency. Thus, apart from the coagulation related charge effects, the particle (floc) size and density which are determined by the flocculation process, play a highly important role in determining the down-stream process efficiency. Under optimal process conditions for DAF and sedimentation no statistically significant efficiency difference was observed for the removal of particles (algae), while the achieved turbidity removal was significantly better by sedimentation than by DAF.

Application of relatively low doses of cationic polyelectrolyte (Superfloc C-573) as coagulant aid (0.5 for DAF and 1.0 mg Superfloc C-573/L for sedimentation) in combination with previously optimised coagulant doses and flocculation conditions, increased process efficiency of both processes (without down-stream filtration) up to 99%. Together with an improved removal efficiency achieved by coagulation at low pH (pH 6 vs. pH 8), this suggests adsorption coagulation and charge neutralisation are the main coagulation mechanisms that support the dosage dependant sweep coagulation and improve the overall particle (algae) removal.

Results from bench scale experiments with model water and laboratory cultured *M. aeruginosa* showed that sedimentation or DAF alone is insufficient to cope with moderate to high initial concentrations of this species. Maximum particle (algae) removal efficiency achieved under optimal process conditions was 71% for DAF (3 mg Fe(III)/L, G=10 or 70 s^{-1}, t=10 min), and 87% for sedimentation (10 mg Fe(III)/L, G=30 s^{-1}, t=30 min). An integrated approach including the up-stream agglomeration (coagulation/flocculation) step, as well as the down-stream filtration step is essential. Adding a non-optimised filtration step in the experimental set-up increased removal efficiency in both cases, for DAF up to 90% and for sedimentation up to 95%. The filtration efficiency in this case (small scale filters connected to the jar test apparatus) was generally influenced by the flocculation G value and the resultant floc size/density ratio. It is also speculated that given the relatively low model water TOC of ≈2.5 mg/L, the residual coagulant (after DAF or sedimentation) is utilised in the filter in a “direct filtration” mode. Thus, the relatively low residual coagulant concentrations (from the point of view of direct filtration) result in relatively low filtration efficiencies. The filtration efficiency itself increased with the residual coagulant increase. Additionally, this situation may be negatively influenced by the (small) scale of the filters - filter wall effects and the non-ripened state of the filter, a situation which will be improved if a fully optimised filtration step is applied.

**REFERENCES**


**APPENDIX 3.1**

Composition of the algae cultivating medium (Jaworski) used for semi-continuous culturing of *M. aeruginosa*.

<table>
<thead>
<tr>
<th>ELEMENTS :</th>
<th>CONCENTRATION (μM) :</th>
<th>TRACE ELEMENTS :</th>
<th>CONCENTRATION (μM) :</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>84.67</td>
<td>B</td>
<td>40.0</td>
</tr>
<tr>
<td>N</td>
<td>163.00</td>
<td>Mn</td>
<td>7.00</td>
</tr>
<tr>
<td>K</td>
<td>91.10</td>
<td>Fe</td>
<td>5.60</td>
</tr>
<tr>
<td>P</td>
<td>191.70</td>
<td>Mo</td>
<td>0.81</td>
</tr>
<tr>
<td>Mg</td>
<td>203.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>203.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>200.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1213.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VITAMINS :</th>
<th>CONCENTRATION (mg/L) :</th>
<th>COMPLEXING AGENTS:</th>
<th>CONCENTRATION (μM) :</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-12</td>
<td>0.04</td>
<td>EDTA Fe Na</td>
<td>5.60</td>
</tr>
<tr>
<td>B-2</td>
<td>0.04</td>
<td>EDTA Na</td>
<td>6.04</td>
</tr>
<tr>
<td>Biotin</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CULTURING PROCEDURE**:

The nutrients were added into 1 L of demineralised water at pH 7, followed by autoclave for a period of 20 min at 120°C. The vitamins solution which had been previously sterilised by filtration at pH 7, was added to the medium afterwards. The incubation of algae (80 mL of *Microcystis aeruginosa* suspension at the end of the logarithmic growth phase) was done in 5 L glass vessels (Duran 50, Schott Mainz, Jena, Germany) at 20°C. The algae suspension was aerated with compressed air passed through a sterile 0.2 μm filter, while continuous mixing was applied at the bottom of the vessel with a magnetic stirrer. The light cycle was continuous at light intensity of ± 1,000 lux. For this purpose a vertically placed T.L. lamp Osram-Cool White L18 W20 was used, placed at a distance of 0.2 m from the walls of the vessel. The stationary algae growth phase was reached after an incubation period of 14-17 days, after which 2 L of the algae suspension were sampled in sterile conditions and used in experiments. The abstracted 2 L of algae suspension were substituted with fresh medium and incubated under the same conditions for 7-10 days, after which algae were sampled for experiments again. This completed the culturing cycle, after which a new culture was started-up.
Chapter 4

POLYELECTROLYTE ENHANCED COAGULATION AND ALGAE CONDITIONING BY OZONE OR KMnO₄ IN THE CONTEXT OF EFFICIENT DISSOLVED AIR FLOTATION

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ABSTRACT: The research investigated ways to improve particle (algae) coagulation and down-stream dissolved air flotation (DAF) removal, by particle (algae) conditioning. The application of organic and synthetic polyelectrolytes, of cationic, non-ionic and anionic charge nature was investigated. The polyelectrolytes were applied as sole coagulant or as coagulant aid with Fe(III) primary coagulant. Bench-scale experiments on model water (tap water spiked with laboratory cultured algae) confirm that cationic polyelectrolytes inducing charge neutralisation and the adsorption-coagulation mechanism are superior to anionic and non-ionic polyelectrolytes associated with the bridging mechanism. The application of oxidants was investigated for the same purpose. Ozone and KMnO₄ improved the particle (alga) removal. Ozone doses as low as 0.2 mg O₃/mg C (0.48 mg O₂/L) increased the DAF process efficiency. Similarly, 0.7 mg KMnO₄/L resulted already in improved DAF process efficiency, however with lower reproducibility and the drawback of high Mn residual, mainly caused by the colloidal MnO₂ with an accompanying turbidity increase. Chemical modifications of the algal cell layer, and the production of in-situ coagulant aid caused by extra-cellular organic matter (EOM) release and in some cases intra-cellular organic matter (IOM) leakage, are considered to be the major process mechanisms responsible for the efficiency improvement. Cationic polyelectrolytes had a positive impact on DAF process efficiency in a combination of ozone or KMnO₄ with inorganic coagulant, as well as in combination of ozone or KMnO₄ with the polyelectrolyte as sole coagulant. The dual coagulant system lowered the overall coagulant demand and reduced the coagulant and Mn residual concentrations. The polyelectrolyte coagulant alone proved to be more sensitive to the ozone dose, but avoided any metal coagulant residue.

4.1 INTRODUCTION

4.1.1 Algae laden water treatment

The variety and the severity of problems related to the treatment of algae laden water originates from the wide diversity of algal species, as well as from their seasonal composition and concentration variations. The differences in their morphological and physiological characteristics include size, shape (form), cell surface characteristics (composition and charge), mobility, extra-cellular organic matter (EOM) production and excretion, growth stage, ability to quickly respond to nutrient composition and concentration changes. This can result in ‘blooms’, excessive concentrations of certain algal species, and periodically results in lower removal efficiency of water treatment. It has been attempted to describe algae removal by approaching them as inert particles and applying the classical coagulation theory whereby they can be destabilised, aggregated and thus brought in filterable form [1]. However, the great diversity of algae accounts for the very different responses to their removal. This calls for a more complex and integrated approach, requiring the establishment of combinations of conventional and advanced treatment unit operations that are suitable for particular circumstances. Membrane technology suggests it can cope efficiently with the problem of high algae concentrations. However, little specific experience is available. Although membranes would in principle be able to remove even the small µ-algae (in the size range of 1 µm), the fact that the very high algae concentrations encountered during blooms generally clog rapid filters and microstrainers, suggests similar problems may occur with membranes.
Conventional water treatment processes for algae laden water usually comprises sedimentation or dissolved air flotation, followed by filtration. The selection of either of the two first processes depends on evaluation of cost and performance, carefully assessed on a per case basis [2]. A bench scale study on model water (with laboratory cultured *Microcystis aeruginosa*) showed a two to three times lower coagulant demand for the optimal algae removal by DAF (3-5 mg Fe(III)/L coagulant) compared to sedimentation (10 mg Fe(III)/L coagulant) [3]. This means lower sludge production and higher solids content. The removal efficiency of dissolved, colloidal and particulate matter in sedimentation, flotation or filtration is primarily defined by the agglomeration (coagulation and flocculation) step. Particle coagulation and flocculation may also prove to be of considerable importance in membrane filtration technology. Depending on pores size, coagulated and flocculated matter may foul the membrane surface, rather than allowing penetration and clogging of membrane pores by suspended and colloidal matter. This suggests easier membrane cleaning [4]. Clearly, ‘optimal’ coagulation conditions are defined by the down-stream treatment process.

Optimisation of the flocculation of model water (*M. aeruginosa*) via DAF jar tests, resulted in relatively poor algae removal efficiencies in the range of 50-70% (Chapter 3) [3]. Control of pH (pH < IEP) and application of cationic polyelectrolytes increased the removal efficiency to the 99% range, confirming the importance of coagulation conditions. Based on the same rationale, algae conditioning by oxidants such as ozone and KMnO₄ should be considered.

4.1.2 Coagulation with metal salts

The stability of mineral and organic particles is attributed to electrostatic charge interactions, hydrophilic effects, or to steric interactions from adsorbed macromolecules [5]. Coagulation with metal salts causes destabilisation of colloidal suspensions by changing the colloids’ surface charge, or by physically destabilising them through encapsulation in large precipitating metal-hydroxide flocs. It is a conditioning process during which the concentration, composition, particle size and particle volume distribution are modified for more efficient down-stream solid-liquid separation by sedimentation, dissolved air flotation, or filtration. The natural organic matter (NOM) which consists of a mixture of various hydrophobic (negatively charged humic and fulvic acids due to carboxylic and phenolic groups comprises about 45% of DOC in rivers) and hydrophilic compounds, rather than the particles, controls the coagulant dose and selection [5]. Coagulation with metal coagulants can also facilitate the conversion of dissolved natural organic matter or molecules (NOM) into insoluble metal-organic products, which are presumably easier to remove physically. The metal-organic reaction products are formed via NOM-coagulant co-precipitation reactions, sorption of NOM onto precipitated coagulant, or combination of these two mechanisms [6]. However, even at very high coagulant doses, a portion of 5-60% of the total NOM is not affected by coagulation [7], presumably due to lack of functional groups capable of coordinating with the hydroxide surface [8].

Iron and aluminum salts are the most common coagulants due to their price and availability, as well as their high efficiency [9]. In the Netherlands, iron coagulants are preferred because of health and environmental concerns related to aluminium. The destabilisation of colloidal and particulate matter and the dominant NOM-coagulant interaction mechanisms are affected by
a range of factors including the water quality (ions concentration and composition, temperature related viscosity, nature and concentration of colloidal and particulate matter, NOM origin, etc.), coagulant type and dose, and coagulation pH [9, 10].

When introduced into water, iron and aluminum salts undergo a series of very fast hydrolytic reactions. In the case of iron, these reactions result in the formation of the initial monomeric hydrolysis products of Fe(OH)\(^{2+}\), Fe(OH)\(^{3+}\) and Fe(OH)\(_3\). The continuing process of nucleation or polymerisation of the monomeric Fe(OH)\(_3\) into amorphous polymeric Fe\(_n\)(OH)\(_{3n}\) results into precipitation and enmeshment of colloidal and suspended matter within these precipitates [10]. The coagulation pH defines the concentration and composition of the metal hydrolysis products and their solubility. The precipitation of metal hydroxide species with enmeshment of impurities is referred to as sweep coagulation, as opposed to adsorption coagulation resulting from surface charge neutralisation followed by particle agglomeration. Although sweep coagulation often is the dominant coagulation mechanism under regular water treatment circumstances, adsorption coagulation is more efficient if one considers the effect per amount of added coagulant. However, it requires adjustment of the coagulation pH below, but close to the iso-electrical point (IEP), i.e. the point of zero average surface charge of the iron hydrolysis products. This enhances flocculation of the negatively charged colloids by the positively charged iron hydrolysis products [3, 11, 12]. The coagulation pH affects the resulting particle (floc) size distribution after flocculation and hence significantly affects the down-stream removal efficiency (Chapter 3) [13]. The IEP for iron-hydroxo complexes is most frequently reported to be in the acidic pH range (between 6 and 7) [9, 14], and strongly influenced by the ionic content and composition of the water (notably Ca\(^{2+}\), HCO\(_3^-\), SO\(_4^{2-}\), HPO\(_4^{2-}\)) [12, 14, 15]. These ions can shift the IEP to lower or higher values or even prevent charge reversal. The colloid concentration usually affects the coagulant dose in an inversely proportional manner when sweep coagulation dominates [16], but a stoichiometric relation tends to exist with spherically shaped algae such as the cyanobacterium *Synechocystis miniscula* (mean diameter of 3 \(\mu\)m, similar to the lower size range of single cell *M. aeruginosa*) in adsorption-coagulation conditions [11]. Drinking water treatment for floc removal with sedimentation or DAF occurs with sweep coagulation given the slightly alkaline pH values under natural circumstances.

4.1.3 Coagulation with polyelectrolytes

Polyelectrolytes or polymers are sometimes applied as single coagulants, but more often as coagulant aids in conjunction with either alum or ferric chloride [8]. Together with metal coagulants they can facilitate conversion of soluble NOM molecules into insoluble NOM-coagulant reaction products, either through precipitation of NOM or sorption of NOM molecules onto the surface of suspended particles. When low molecular weight (MW) cationic polymers are added to a solution, precipitation is the only likely mechanism of soluble NOM removal [6].

The chemical structure of natural or synthetic polyelectrolyte molecules is characterised by repeating (monomer) chemical units in a branched or linear manner. Their molecular weight is usually \(10^4 - 10^7\), and they are water soluble due to hydration of their functional groups. The
polymers carry an overall cationic or anionic charge, or they may be non-ionic [10]. The charge, and adsorption characteristics define the particle destabilisation capacity, the most relevant for drinking water treatment being the bridging and the adsorption coagulation mechanisms which in some cases operate simultaneously [10, 17]. The first mechanism is based on the presumption that the polyelectrolyte molecules are of similar dimension as many of the colloidal particles and operate via adsorption of polyelectrolyte to more than one particle, thus binding the particles together. This may be the case when non-ionic or anionic polyelectrolytes are applied. In the case of anionic polyelectrolytes, the particle adsorption occurs through interaction with metal ions, such as calcium, on the particle’s surface. As for the non-ionic polyelectrolytes, their adsorption to negatively charged particles is mostly via hydrogen bonding. The high efficiency of cationic polyelectrolytes is based mainly on their charge being opposite to that of the colloidal and particulate matter. The strong attraction of polymer and colloidal surface would result in a configuration of the polyelectrolyte molecules lying flat on the particle surface, making the bridging mechanism less likely. Similar phenomena can be expected to occur with anionic and non-ionic polyelectrolytes if the ionic strength of the water is very high. In has been suggested [17] that the polyelectrolyte can assume a localised ‘patch’-like structure on the particle resulting in a mosaic type of charge distribution, with patches of positive and negative charges co-existing on the particle. When oppositely charged ‘patched’ surfaces come into contact with each other, this results in strong inter-particle attachment and agglomeration.

Polyelectrolytes can be very efficient as sole coagulants in the treatment of turbid or coloured water containing humic acids as well as various microorganisms [10]. Polyelectrolytes don’t need major pH adjustment, prevent the carry over of soluble organo-metal complexes to the solid-liquid separation phase, minimise the carry over of light flocs formed in the case of metal coagulant application, and finally reduce the sludge volume and the amount of soluble anions. These advantages promoted intensive use of synthetic polyelectrolytes, notably in the USA [18]. Disadvantages pertain to their high degree of selectivity for certain types of colloids, high unit cost, poor biodegradability for synthetic polyelectrolytes, and uncertainty regarding carcinogenicity and mutagenicity of their monomers [18]. This is compounded by the absence of an appropriate analytical methodology for their quantification, as well as of data on their exact chemical structure. However, natural polyelectrolytes such as chitosan (cationic) and sodium alginate (anionic) can be as efficient as synthetic ones, without the related toxic hazards [18]. This has resulted in a cautious approach to polyelectrolyte application in many countries including the Netherlands where officially only one non-ionic and one anionic organic (starch based) polyelectrolyte is currently approved.

Therefore, the application of natural polyelectrolytes, as well as lower polyelectrolyte doses seems attractive. Numerous cases of improvement of solid-liquid separation efficiency by small concentration of coagulant aid have been reported [3, 18, 19, 20, 21, 22, 23]. Their application typically leads to larger, but also denser floc material (Chapter 3) [13]. One of the main advantages is the accompanying reduction of prime coagulant dose requirement. The appropriate polyelectrolyte needs to be determined on a case to case base, depending on the raw water quality. Anionic and non-ionic polyelectrolyte coagulant aids have been proven efficient mostly for sedimentation where relatively large mineral coagulant doses induce sweep coagulation; by increasing the overall particle concentration they introduce surface area for the
bridging mechanism. However, cationic polyelectrolytes have generally been recognised as more effective. For coagulation of humic substances, bacteria and algae they are considered the only option [21]. In the case of cationic coagulant aid, the sweep coagulation is significantly aided by the polyelectrolyte induced adsorption coagulation. This option is attractive if pH reduction below the IEP is not feasible, for example due to high buffering capacity [22].

Critical in the use of polyelectrolytes is the mixing intensity in the coagulation unit. Velocity gradients (G values) of 400-1,000 s⁻¹ have been recommended. Larger values possibly give rise to floc break-up, while lower values provide for insufficient contact opportunities. The polyelectrolyte dose may also affect the optimal velocity gradient value, and is generally inversely proportional [10].

The application of cationic polyelectrolytes in the DAF saturation unit has been shown to cause coating of air bubbles with these polyelectrolytes. This may result in increased particle removal efficiency, based on more intensive attraction and efficient adsorption between negatively charged particles and coated positively charged air bubbles [23].

4.1.4 Conditioning with oxidants

Numerous experiences at both, laboratory and operational scale [22, 24, 25, 26, 27, 28, 29], suggest that oxidants conditioning enhances coagulation. These effects accompany the primary disinfectant role of most of the oxidants including chlorine, chlorine dioxide, ozone and potassium permanganate. They are caused by chemical interactions between the oxidant and the dissolved, colloidal and particulate matter (including algae). However, hazardous oxidation by-products are associated with certain oxidants, such as trihalomethanes (THM), haloacetic acids (HAA) and haloacetonitriles (HAN) with chlorine, chlorite with chlorine dioxide, and bromate with ozone [30]. The formation of these by-products is influenced by a range of factors; careful setting of, for example ozone dose or ozonation pH, allow to maintain bromate levels below the guideline values [31, 32, 33]. The application of advanced oxidation processes where combinations of oxidants is considered, may result in improved process efficiency at reduced health hazard risks [34].

The process kinetics of coagulation enhancement by oxidant conditioning depends on the oxidant, its dose, and the raw water quality characteristics. In case of ozone conditioning a series of chemical reactions takes place with a net positive or negative effect on the coagulation process. The process mechanisms of ozone induced coagulation improvement include [35]:

- reactions with NOM leading to a decrease of their molecular weight and increase in their functional group content, and resulting increase of sorption of these compounds on metal-hydroxide flocs;
- increased complexation of calcium with NOM;
- reduced particle stability, due to ozone reacting with the NOM coating the colloids;
- break-up of organo-metal complexes, yielding coagulant in-situ;
- reactions of ozone induced meta-stable ozonides, peroxides and free radicals with NOM,
after the initial ozone has been depleted;
- immobilisation of zoo- and phytoplankton (especially motile algae), and disruption of their 
metabolic processes;
- reactions with functional groups on alga cell surface reducing cell surface charge, as well as 
production of surface active substances which behave as biopolymers and natural coagulant 
aids.

As for KMnO₄ conditioning, coagulation is facilitated by similar mechanisms as far as 
reactions with the NOM and algae are concerned, but the effect includes the additional benefits 
caused by the formation of the colloidal hydrous MnO₂. The MnO₂ can improve coagulation 
efficiency by increasing the overall particle concentration and aiding the sweep coagulation, 
by acting as an adsorption agent for organic and inorganic matter, and by adsorbing on algal 
cells and assisting their further coagulation by metal coagulants [36].

THM formation discredited chlorine based oxidants in the seventies. Ozone gained 
considerable attention in the eighties, especially in the USA and France. However, the 
establishment of a relation between ozone and the formation of brominated organohalogens or 
bromate in bromide containing water at potentially hazardous levels, reflected negatively on 
this technique [32, 33, 37, 38, 39]. The formation of bromate is significantly influenced by 
the ozone dose and ozonation pH which may prove to be decisive for its feasibility [30, 32, 
33, 34, 39]. Furthermore, the application of ozone raises the assimilable organic carbon 
(AOC) in the treated water, and if no additional retention measure for AOC is present before 
the distribution network, this may result in bacterial after-growth [39, 40]. If such a barrier, 
e.g. in the form of granular activated carbon (GAC) filtration exists, ozone will improve the 
biodegradability of the organic matter and thus may prove beneficial for GAC filter operation 
[39, 41].

A non-hazardous alternative to ozone is KMnO₄ [22, 30, 42]. This very strong oxidant has 
extensively been used, mainly for taste and odour control, and for Fe(II) and Mn(II) removal. 
It has gained increased attention lately because of its disinfecting and algicidal effects, its effect 
on the trihalomethanes formation potential, and as a particle (algae) conditioner before 
coagulation. However, overdosing of permanganate results in a characteristic, objectionable 
pink colour of the treated water, but this also allows to optimise its application. Apart from 
the high cost, its drawback is the potentially higher residual Mn in the effluent.

Application of ozone or KMnO₄ in combination with polyelectrolytes is proposed to be a viable 
option for further increasing removal efficiency. It has been shown that dual coagulant systems 
(Fe or Al salts in combination with primarily cationic polyelectrolytes) in combination with 
ozone or KMnO₄ perform better than the combination of ozone or KMnO₄ and coagulant alone 
[36]. If one defines a critical coagulant concentration (CCC) as the concentration of each of 
the considered polyelectrolyte and metal coagulant necessary to reach a 0 mV particle charge 
when used separately, their jointed impact is more efficient and not according to the additive 
principle (linear additivity model) [6]. The impact on coagulant demand and solid-liquid 
separation process efficiency depends on the characteristics of the polyelectrolyte and its ratio 
to the Fe or alum salt, under particular raw water circumstances (particle concentration, ionic 
composition, pH, etc.) [6]. Ozone or KMnO₄ conditioning can have an impact on the raw
water quality (e.g. ozone can modify organic matter and influence the DOC composition via EOM and IOM leakage, while KMnO₄ additionally results in MnO₂ production), and thus affect the outcome of the combined polyelectrolyte-metal coagulant treatment in many ways. Efficiency improvement may be caused by i.e. a decrease of the negative particle (algae) charge in the case of ozone conditioning [3, 22, 36, 43], or adsorption of the negatively charged colloidal MnO₂ in the case of KMnO₄ conditioning [22, 36].

4.1.5 Ozone conditioning

Ozone exerts a strong disinfectant activity (inactivation of viruses and other pathogenic microorganisms) [39], and is effective in colour removal, taste and odour improvement, reduction of phenolic compounds and UV₂₅₄ absorbance, whilst the THM formation potential can be reduced [22, 36].

The ozone dose is very critical. It is primarily determined by the NOM content. Coagulation and down-stream process efficiency are known to improve very significantly at ozone doses of 0.3-0.4 mg O₃/mg C (0.5-1.5 mg O₃/L), while higher doses can lead to deteriorated effluent quality [35]. High ozone doses may lead to algal cell break-up and release of IOM comprised of polysaccharides, proteins and nucleic acids into the water, which may in some cases inhibit the flocculation process. The critical ozone dose differs for alga species [25, 43, 44], depending on the outer algal cell wall composition (hence on age) as well as on the raw water concentration and composition of the NOM. IOM leakage may also benefit the flocculation process, since it can serve as a natural coagulant aid.

Raw water quality strongly influences the ozone conditioning. Ozone conditioning of the same water (Seine River, France) at different locations and times resulted in variable, even conflicting results [35]. These differences are mainly the result of variations in NOM concentration and composition. A minimal concentration of organic matter is needed as a prerequisite for the occurrence of the beneficial effect of ozone on coagulation [45]. Seasonal algae blooms and their EOM seem to play a crucial role. Consequently, different species may cause different effects since they respond differently to ozone treatment; for example, some species are considered the cause of the formation of a thick organic foam layer in water treatment plants, due to ozone induced release of surface-active biopolymers [26]. The effect of ozone on particles coagulation is closely related to its reactions with their NOM coating [29]. The surface properties of particles are altered in the sense of changes in the functional group content and an increase of the carboxyl content of NOM. These reactions provoke the formation of organic radicals that may lead to polymerisation reactions. Thus, by changing the surface properties of the particles the reactions with metal coagulants proceed in a different manner, aided by the formed polymers [45]. Ozone conditioning generally shifts the particle size distribution towards larger particles and changes the organic matter phase from dissolved to colloidal, with a positive down-stream flocculation effect.

Ozone application generally decreases the molecular weight (MW) and increases the acidic functional group content and the hydrophilicity of the NOM [6]. This leads to a net decrease of the tendency of NOM molecules to be removed via precipitation reactions with the metal
hydroxide coagulant. On the other hand, the impact of ozone on NOM removal via sorption reactions is more complex; while the increased acidic functional group content would tend to increase sorption, the decreased MW has the opposite effect. Conceptually, the overall affinity of metal-hydroxide surfaces for ionised organic adsorbates may be divided into two components. One component accounts for the non-electrostatic forces between the ion and the surface and depends on their quality. The other component accounts for the electrostatic portion of the affinity, i.e. the repulsion/attraction between the ion and the surface, which is a function of the adsorbate charge and the surface potential (consequently sensitive to pH, ionic strength and the presence of other adsorbates). Thus, the overall coagulation effect will be a net effect of the precipitation and sorption NOM-coagulant reactions. Organic matter (TOC) removal in the case of ozonation is a combined effect of oxidation, stripping and coagulation; It has been found that it improved with increased ozone dose at very high and at low coagulant doses, and it decreased at moderate coagulant doses. Furthermore, the application of ozone in combination with polyelectrolyte coagulants may result in a masked effect of ‘reduced coagulant demand’, which is a result of the transformation of the NOM to lower MW, and the creation of more hydrophilic species, thus decreasing the required polyelectrolyte coagulant dose for NOM precipitation, as the amount of precipitable NOM decreases. The complexity of the ozone induced NOM changes and the variations in NOM concentration and composition at different locations and time explain the often inconsistent data on TOC removal in the literature [6].

Similarly, calcium hardness influences ozone induced changes of the coagulation process. The coagulation of NOM coated particles improves in the presence of divalent cations such as calcium [26, 43, 46]. The effects of Ca$^{2+}$ include adsorption and charge neutralisation through calcium complexation with both, surface functional groups on the metal oxide and with the NOM coating of particles, double layer compression by calcium, and calcium bridging between negatively charged humic matter or solid surfaces. Fig. 4.1 describes the relationship between the influence of the raw water characteristics (hardness and TOC) and the ozone induced coagulating effect, expressed via the particle collision efficiency coefficient $\alpha$. Accordingly, optimal ozone induced coagulation takes place at hardness to TOC ratios larger than 25mg CaCO$_3$/mgC and ozone doses in the range of 0.4-0.8mg O$_3$/mgC [47].
The time lag between ozone application and application of coagulant is also important for coagulation and flocculation efficiency. It has been speculated [36] that the ozone induced flocculation improvement is a reversible process affected by the time lag between ozone and coagulant addition. The shorter it is (in the range of 1-2 min), the better the results from the down-stream (direct) filtration were. This implies that there is no need of large contact units if ozone is applied for conditioning purposes.

It is often difficult to distinguish all occurring phenomena, however, a comprehensive overview of mechanisms involved in the ozone induced algae coagulation improvement includes [36]:

- splitting of EOM molecules;
- alteration and removal of EOM and NOM adsorbed on particles;
- reaction with adsorbed organic coating on algal cell surface, responsible for enhanced algae stability;
- reaction with and modification of the algal cell wall structure resulting in reduction of their stability;
- release of algae IOM (Intracellular Organic Matter) which (further modified by ozone) may act as a natural coagulant aid biopolymer and enhance coagulation.

4.1.6 KMnO₄ conditioning

KMnO₄ conditioning as an option for coagulation improvement has been considered only recently. The application of this strong oxidant dates back to the beginning of this century, mainly to control noxious taste and odour causing compounds [48, 49, 50]. Ever since it has been used also for Mn(II) and Fe(II) oxidation and conversion from dissolved to colloidal form in ground and surface water treatment [48, 51], as an algicide for phyto- and zooplankton growth control in reservoirs [52, 53, 54], and as an oxidant to replace chlorine for THM avoidance [55, 56, 57]. Recent studies on the applicability of permanganate in the context of improved particle coagulation and flocculation have proven its beneficial effect, showing that it may behave as a coagulant aid and substantially improve direct filtration efficiency in particular [22, 42]. Finally, permanganate has also been used for disinfection purposes and for hydrogen sulphide removal [58].

KMnO₄ oxidizes chemical contaminants and biomass [50]. The standard electric potential for the oxidation reaction of permanganate indicates that it can oxidize most inorganic compounds, as well as virtually any organic compound [59]. Its oxidation rate is influenced mainly by pH, temperature and the presence of certain catalytic ions [48]. Under normal pH conditions of 7-8.5, the insoluble hydrous MnO₂ (of 0.3-0.4 μm size [59]) is the end product of permanganate reduction, the reaction rate being higher for pH greater than 7. KMnO₄ owes its overall efficiency to the combined oxidative activity and the adsorption characteristics of its oxidation by-product, i.e. the MnO₂. This applies for particles (algae) conditioning as well. The mechanisms involved in the KMnO₄ induced coagulation and flocculation improvement are similar to those for ozone application, but in addition include the activity of the MnO₂:
- increase of flocculation efficiency due to the increase of overall particle concentration aiding sweep coagulation;
- adsorption of/inorganic and organic matter (including algae), as well as adsorption of cations (and anions) of inorganic and organic origin.

Depending on the formation conditions, a more correct notation of manganese dioxide would be \( \text{MnO}_x \), where \( x \) varies from 0.1-0.95 [60]. The initial (colloidal) size of its precipitate is 0.3-0.4 \( \mu \text{m} \), its surface atoms assuming a well ordered crystal structure with exchangeable hydrogen and hydroxide ions bound on the surface. The hydrous \( \text{MnO}_2 \) is amphoteric, however, under the pH conditions of water treatment it is of negative charge [60]. Its colloidal size and resulting large surface area (about 300 \( \text{m}^2/\text{g} \)) promote it as a very fast and efficient sorption agent, especially for multivalent metal cations and cationic organics. This does not apply for non-ionic and anionic organics [46, 60]. The principal mechanisms underlying the metal and organic ion sorption are ion exchange sorption and direct ion attraction [60]. The ion exchange properties of \( \text{MnO}_2 \) are related to acidic functional groups at its surface, resulting in a weak acid behaviour and a strong dependency on pH (increase of pH resulting in increased negative charge and cation exchange capacity).

The increased residual Mn concentration may limit \( \text{KMnO}_4 \) application to a certain degree. The residual is of characteristic pink colour. \( \text{MnO}_2 \) may impart a dark brown to yellowish colour, dependent on pH. Unlike the permanganate it can presumably be removed by filtration, however, shortening the filter runs. Its size ranks it into a particle category which is difficult to remove by filtration. Cationic polyelectrolytes are reported to improve filtration also via reducing the residual Mn concentrations [36]. As for the permanganate residual, reducing agents such as \( \text{Na}_2\text{SO}_3 \) are proven to be beneficial. However, organic matter deposits on the filter grains material may also exhibit a substantial permanganate demand and act as its reducer [50]. A careful permanganate dosing pattern, e.g. maintaining pink colour in two thirds of the sedimentation tank, may allow for a full utilisation of the oxidizing potential of the permanganate [61], and reduce the necessity of additional chemical permanganate reduction by allowing the filters to satisfy their permanganate demand.

Although application of permanganate may occasionally have a negative impact on the THM formation potential [55], this has little relevance for Dutch drinking water production in which chlorination is not extensively practised. Importantly, presently no direct or indirect hazardous by-products are known to be caused by the permanganate application.

### 4.1.7 Research rationale

Based on the circular shape and size characteristics of the single cell \( \text{M. aeruginosa} \), one of the research goals is to test the existence of a stoichiometric relation between their concentration and the coagulant dose necessary for their optimal destabilisation and downstream DAF removal. The relatively low DAF removal efficiency of algae (\( \text{M. aeruginosa} \)) of 50-70\% achieved in the model water research (Chapter 3), as well as the significant increase (up to 99\%) of the algae removal via coagulation pH control (pH < 7) and cationic polyelectrolyte C-573 coagulant aid, suggest the existence of an operational window for
process operation improvement. For the purpose of DAF process enhancement the application of polyelectrolytes of different charge characteristics and in different modes, i.e. as sole coagulant or coagulant aid in combination with iron coagulant, is to be assessed. In the latter case, polyelectrolytes will be applied in order to test the possibility of raising the Fe(III) coagulant efficiency. The process efficiency is to be assessed in terms of the polyelectrolytes' charge and weight characteristics. Another option for DAF process enhancement which is to be studied is conditioning with oxidants, i.e. ozone and KMnO₄. The feasibility of the following treatment enhancement options is to be addressed in the research: (i) combined treatment by (iron) coagulant and oxidant conditioning, (ii) (iron) coagulant, polyelectrolyte coagulant aid, and oxidant conditioning, and (iii) polyelectrolyte coagulant and oxidant conditioning. Different coagulant, oxidant and polyelectrolyte dose combinations will be tested in the context of maximising DAF process efficiency and minimising chemicals consumption. The research will also address and investigate some oxidant specific aspects like: oxidants imparted microfloculation phenomena, point of (metal) coagulant dosing relative to the oxidant, temporal algae concentration variation and reduction of KMnO₄ by Na₂SO₃.

The research aims at providing deeper and more comprehensive insights into the factors that affect the removal efficiency of algae and the governing process mechanisms. The impact of different treatment combinations is to be assessed by turbidity, particle count, residual coagulant, UV absorbance at 254 nm, and algae and floc surface charge measurements, while computer image analysis will provide insight into (micro)floculation phenomena. Scanning electron microscopy (SEM) is to be used to assess the impact of ozone on the algal cell structure. The research will also consider and assess the potential risks related to the application of these treatment enhancement technologies. The outcome should be the provision of a more solid knowledge basis for their eventual application in the context of solving short and long term algae treatment problems.

4.2 MATERIALS AND METHODS

4.2.1 Experimental set-up

The laboratory bench-scale experimental set-up consisted of a jar test apparatus with incorporated DAF facilities (Fig. 3.1). The recirculation ratio in the DAF unit was 7%, while the saturator pressure was 500 kPa. The experimental procedure included coagulation at a pH 8, temperature of 20 °C and G of 1,000 s⁻¹ for 30 s. Based on previous experimental work the floculation G was set at Gₜ=10, 30 or 70 s⁻¹ and the floculation time at tₜ= 10 or 15 min. FeCl₃·6H₂O was used as coagulant. The dose range for the optimisation of algae removal and testing for the existence of stoichiometry between algae concentration and optimal removal coagulant dose was 0-15 mg Fe(III)/L. Based on the analysis from Chapter 1, the selected cyanobacterium species was a semi-continuously, laboratory cultured, single cell form of *M. aeruginosa* (see Appendix 3.1 for details on culturing conditions) spiked into water originating from the Biesbosch storage reservoirs (North Brabant, the Netherlands) to different initial concentrations of = 5,000, 10,000, 15,000, 20,000 and 25,000 ±cells/mL. The optimal coagulant dose is defined as the dose at which highest particle (algae), turbidity and coagulant removal takes place.
Four brands of polyelectrolytes were tested as coagulants and as coagulant aids. Two of these were of synthetic (cationic Superfloc C-573 and anionic Superfloc A-100) and two of organic (cationic Wisprofloc-P and non-ionic Wisprofloc-N) nature. Superfloc C-573 is a quaternary amine based, low molecular weight, cationic polyelectrolyte of 50% active matter, used in the 1.0-10.0 mg/L dose range as sole coagulant and 0.05-1.0 mg/L as coagulant aid. Superfloc A-100 is a high molecular weight polyacrylamide based anionic polyelectrolyte of 100% active matter applied in the dose range of 0.2-10.0 mg/L as sole coagulant and 0.05-1.0 mg/L as coagulant aid. The Wisprofloc-P is a soluble potato starch derivative cationic polyelectrolyte applied in a dose range of 0.25-5 mg/L as coagulant or coagulant aid. The Wisprofloc-N is of similar origin and characteristics as the Wisprofloc-P, however it is non-ionic. Polyelectrolytes were prepared in accordance to manufacturers recommendations. This was accomplished by dissolving the liquid or powder polyelectrolyte into demineralised water before each set of experiments (to avoid problems caused by polyelectrolyte aging and inactivation). The preparation of working and stock solutions was done in plastic utensils to avoid loss of polyelectrolyte due to wall adhesion. The use of polyelectrolytes as sole coagulants was tested in a dose range of 0.2-3 mg/L and included rapid mixing at a G value of 500 s\(^{-1}\) for 30 s, while the flocculation followed the same pattern as in the case of metal coagulant application. The application of polyelectrolytes as coagulant aids was done in the dose range of 0.1-1.0 mg/L, under the same coagulation G and t conditions, following the application of the previously optimised primary metal coagulant dose (Chapter 3). Tests were limited to polyelectrolyte combinations with the optimal Fe coagulant dose due to time limitations.

For ozone production in the conditioning experiments the Trailigaz LABO LO, France, ozone generator was used. Ozone was produced under standard ozone generator conditions of 220 V, 0.6 A, and 0.6-0.7 bar pressure. The raw water hardness (as CaCO\(_3\)) to TOC ratio was in the range of 65-70 and thus >25, a value suggested to warrant ozone induced coagulation/flocculation improvement. Most of the TOC was in the dissolved form (DOC=80% of TOC). Based on the model water TOC concentration for the 10,000 cells/mL algae concentration which was measured prior to each ozone experiment (mean value of 2.4 mg C/L), and the prescribed ozone dose range for improved coagulation/flocculation of 0.4-0.8 mg O\(_3\)/mg C [47], three ozone doses were applied. A lower (0.2 mg O\(_3\)/mg C), within the prescribed range (0.5 mg O\(_3\)/mg C), and a higher (0.9 mg O\(_3\)/mg C) ozone dose were applied, while in some specifically mentioned cases a high dose of 1.3 mg O\(_3\)/mg C was also applied. The ozone dosage (transferred ozone) was derived from the ozonation time which was varied from 1-4.5 min. The pH of the raw (model) water subject to ozonation was previously set to 7.5 by HCl addition.

A 5.5 L ozone resistant glass jar was used as a batch ozone reactor. The time gap between ozonation and subsequent coagulation/flocculation was kept at 2 min, in order to comply with previous positive experiences with short time gaps [36]. The pH change after ozonation was 7.5±0.2 and it served as coagulation pH without additional corrections. Ozone was applied in combination with the previously determined optimal coagulant dose for a concentration of =10,000 cells/mL of M. aeruginosa (3 mg Fe(III)/L), as well as with a 50% lower (1.5 mg Fe(III)/L) and a 50% higher (4.5 mg Fe(III)/L) coagulant dose. The same strategy was applied for a =5,000 cells/mL M. aeruginosa concentration (ozone combined with 1, 2 or 3 mg Fe(III)/L). The cationic polyelectrolytes Superfloc C-573 and Wisprofloc-P were tested as sole coagulants (0.3-1.0 mg/L), or as coagulant aids (0.1-1.0 mg/L) to Fe(III) coagulant, combined with a low (0.2 mg O\(_3\)/mg C) and high (0.9 mg O\(_3\)/mg C) ozone dose.
For permanganate conditioning experiments a 0.0057 M stock solution was prepared at weekly intervals. The applied permanganate dose ranged from 0.1-2.0 mg KMnO₄/L, while the pH was previously set at 8. The permanganate was applied at a G value of 400 s⁻¹ for a period of 1 min, followed by 30 min of slow mixing at a G value of 10 s⁻¹. This rather long contact time before coagulant application was applied in order to simulate conditions under which permanganate is dosed as soon as possible within the treatment process. The positive effect of this strategy is the long time available for permanganate reactions before coagulant application, but in practice some MnO₂ would precipitate on the tank and channel walls. Thus, previous to all experiments, the precipitation rate of permanganate and formation of MnO₂ was assessed within the adopted 30 min contact time. Measurements of both dissolved Mn(VII) and particulate Mn(IV) were conducted for each experiment. The optimisation of the KMnO₄ dose was based on the visual determination technique (no pink colour observable in the DAF effluent). It was combined with a previously optimised Fe(III) coagulant dose at coagulation pH 8. The impact of the conditioning pH (6, 7, 8, and 9) on DAF efficiency was also tested. The flocculation G (10, 30, 70 and 130 s⁻¹) and t (10, 15, 20 and 30 min) were varied in search for the existence of an optimal Gt range. An overview of the experimental conditions for each of the particular sets of experiments is given in Appendix 4.1.

4.2.2 Analytical techniques.

Process efficiency was evaluated by turbidity (Sigrist L-65, Switzerland) and particle (alga) count of particles > 2.75 µm (HIAC-Royco PC-320, USA). A Nikon Optiphot (Japan) microscope was used for sample inspection. Residual coagulant (Fe₉₀₆) and manganese were measured by atomic absorption spectrometry at 248.3 nm for iron (NEN 6460) [62] and 279.5 for manganese (NEN 6466) [63]. Electrophoretic mobility was measured with a Tom Lindström AB-Repar apparatus. Transferred ozone was determined by measuring the O₂ concentration in the inlet and outlet air/ozone gas mixture by the iodometric method [64]. Computer image analysis was performed with the Mini-Magiscan (IAS 25/IV25 Joyce-Loebli Ltd., UK) [13].

Scanning electron microscopy (SEM) was performed with a JEOL 6300 F microscope; samples were previously filtered (0.22 µm) to remove surrounding water but leave algae cells intact by avoiding dehydration. Prior to SEM samples were frozen in liquid nitrogen and mounted into a cryo-transfer unit (CT 1500 HF, Oxford Instruments, UK) under high vacuum (1x10⁻⁸ Pa), temperature of -85°C and sputter coated (Denton) with 3 nm platinum. SEM observation of the coated specimen was carried out at 5KV and -180°C.

Statistical analysis of data was performed with the Statistica software package. One and two way ANOVAs followed by multiple comparison and regression analysis among treatment.

4.3 RESULTS AND DISCUSSION

4.3.1 Stoichiometry between algae concentration and metal coagulant dose

Stoichiometric relationships between alga concentration and coagulant dose were found to apply for spherically shaped, single cell µ-algae [11]. This suggests that these algae can be considered as behaving as inorganic particles to which the common coagulation and flocculation
theory applies. This does not apply, however, for algae which have particular morphological features such as bristle-like appendages (*Stephanodiscus hantzschii*) or a mucilaginous sheath layer around the cells (*Dictyosphaeriurn*). The size and shape of the single cell form of *M. aeruginosa* suggest a linear stoichiometric relation may exist. DAF jar tests with model water (spiked with different concentrations of laboratory cultured algae), in which the coagulant dose was optimised confirmed the existence of such a relationship (Fig. 4.2). The regression line is a polynomial, suggesting that at a certain point (high algae concentrations above 20,000 cells/mL) there is no need for further coagulant dose increase. Possibly, a critical concentration of coagulant (8-9 mg Fe (III)/L) has been reached which allows for sweep coagulation, i.e. destabilisation to occur without further increase of the coagulant dose. According to classical coagulation theory the coagulant dose is inversely proportional to the concentration of aquatic colloids at high colloid concentration, as is here the case at and above 20,000 cells/mL [16].

Even at the highest coagulant dose, EM (electrophoretic mobility) did not show particle charge neutralisation (or reversal) in the presence of the algae. However, adding coagulant to water without algae resulted in charge neutralisation (of Fe(OH)₃ particles) and reversal at a dosage of 15 mg Fe(III)/L (Fig.4.3). The charge reversal in the water without algae could be attributed to gradual elimination of HCO₃⁻ by H⁺, generated by Fe(III) hydrolysis. High Ca²⁺ concentrations (here 150-200 mg as CaCO₃) accompanied by a very low HCO₃⁻ level tend to shift the IEP of Fe(OH)₃ from pH 6-7 to slightly alkaline values, as is the case here [14]. The algae spiked water, on the other hand, would have a substantially different composition with respect to ions and organics, because it contains the growth medium of the algae culture (see Appendix 3.1). Although it would be very difficult to identify the responsible compounds the net effect appears to result in a shift in IEP precluding charge reversal at pH 8.
4.3.2 Polyelectrolytes in coagulation

a. Polyelectrolytes as coagulant aid

Earlier work on the importance of the coagulation pH (Chapter 3) resulted in significantly improved coagulation and down-stream DAF efficiency at pH ≤ 6. This is likely to be owed to a combination of partial adsorption coagulation, which occurs at pH below the IEP, and sweep coagulation [3]. In practice, however, it is very often not feasible to correct pH. However, the role of adsorption coagulation suggests cationic polyelectrolytes may be also effective to achieve adsorption coagulation. The cationic polyelectrolyte Superfloc C-573 was proven to be a coagulant aid highly beneficial to DAF (and sedimentation) efficiency, resulting in 94.5% particle (alga) removal, improved turbidity removal and reduced residual coagulant content. In further research different types of organic and inorganic polyelectrolytes of different chemical composition, charge and weight characteristics were considered. Figs. 4.4 and 4.5 represent particle (alga) and turbidity removal efficiency for different types and doses of polyelectrolyte coagulant aid.

**Fig. 4.4** Particle (alga *M. aeruginosa*) removal efficiency by DAF for different types and doses of polyelectrolyte. Conditions: ≈ 10,000 cells/mL, initial turbidity of 3.85 FTU, 3 mg Fe(III)/L, pH 8, G = 30 s⁻¹, tᵣ = 10 min, R = 7%, p = 500 kPa.

**Fig. 4.5** Turbidity removal efficiency by DAF for different types and doses of polyelectrolyte. Conditions: same as Fig. 4.4.
The synthetic cationic polyelectrolyte Superfloc C-573 was the most efficient. These results confirm other positive experiences with polyelectrolyte coagulant aids and Scenedesmus spp. algae removal [65]. However they contradict other findings in which synthetic cationic polymers were used as coagulant aid together with Fe(III) coagulant for the removal of M. aeruginosa (100,000 cells/mL concentration) and were found inefficient [66]. Other low molecular weight cationic polymers (Catfloc T2 and Catfloc TL, at dosages of 2-3 and 5 mg/L in combination with 30 and 16.5 mg Fe(III) coagulant respectively) were efficient for DAF algae removal [67]. Superfloc C-573 owes its efficiency to the very strong charge characteristics which resulted in particle (algae) charge neutralisation as verified by EM measurements (Fig. 4.6). Similar charge neutralisation effects were noted for the organic cationic polyelectrolyte Wisprofloc-P, however, of lower accompanying process efficiency. The same polyelectrolyte was again inefficient for the DAF treatment of Stephanodiscus spp. (36,000 cells/mL) [66], while it efficiently reduced DAF effluent turbidity (5 FTU before, and 1.2 FTU after its application) and residual alum (from 400 to 20 µg/L) in other circumstances [68]. This indicates additional factors as relevant for the noted process efficiency. Two such factors are the resultant floc size (distribution) and density. The floc volume distribution has been indicated as dependant on the polyelectrolyte configuration, since it is critical for their adsorption to particulates (and media in filtration) [69].

![Electrophoretic mobility (EM) of particles for different types and doses of polyelectrolyte. Conditions: 3 mg Fe(III)/L, pH 8, G=30 s⁻¹, t_r=10 min, R=7%, p=500 kPa.](image)

One way ANOVAs for the effect of different dose of Superfloc C-573 coagulant aid on the particle (alga) and turbidity removal efficiency showed that both were statistically significantly affected by treatment with coagulant only, as compared with coagulant and coagulant aid (P=0.00000 for particle count and P=0.012 for turbidity). One way ANOVA for the initial particle (alga) count showed that the initial conditions were similar for all experiments (P=0.99), while for turbidity it was not the case (P=0.00054). The difference which was found for initial turbidity between the case of coagulant only and that of coagulant and coagulant aid, is due to the difficulty to prepare identical algae cultures (see Chapter 3, Fig. 3.2). However, including initial turbidity and particle count as covariates in the analysis, showed that both the turbidity and particle removal efficiency were significantly affected by the polyelectrolyte (P=0.00000 for particle count and P=0.000084 for turbidity).
The optimal polyelectrolyte dose in terms of DAF (and sedimentation) efficiency was in the range of one tenth of the coagulant dose. Particle size analysis after flocculation with the Superfloc C-573 as coagulant aid [3, 13] showed that the increase of polyelectrolyte dose from 0.5 to 1.0 mg C-573/L resulted in the production of floc material of denser structure (Fig. 3.8, Chapter 3). The long polyelectrolyte chain structure of the Wisprofloc-P is suggested responsible for the observed formation of floc material larger than in case of the Superfloc C-573. Although no particle size analysis was done in case of the Wisprofloc-P, the floc size visibly increased with the polyelectrolyte dose, opposite to the case of Superfloc C-573. Furthermore, the Wisprofloc-P based floc material tended to stick to the walls of the jars, as well as to other surfaces like the stirrer. The algae were destabilised and flocculated, however, the floc quality (size and density) was not appropriate for DAF. The polyelectrolyte dose increase had a pronounced effect on the turbidity, which rose with the Wisprofloc-P dose, contrary to the case of Superfloc C-573 (see Fig. 4.5). The increased turbidity levels suggest high residual polyelectrolyte concentrations. The absence of a residual polyelectrolyte characterisation technique, precludes discerning the extent to which they affect the residual turbidity, as well as to assess the potential health hazards.

The anionic polyelectrolyte Superfloc A-100 and the non-ionic Wisprofloc-N proved inefficient under the tested circumstances. The DAF effluent deteriorated in comparison with the case when Fe(III) was used as sole coagulant, the removal efficiency for both polyelectrolytes being below 50%. In the case of Superfloc A-100, this was accompanied with a slight increase of turbidity removal, whereas the turbidity increased in the case of Wisprofloc-N. Similar observations pertain to residual iron, which was relatively low in the case of Superfloc A-100 (removal rate of 75-85%). The EM measurements show no significant changes; particles become slightly more negative in the case of Superfloc A-100, and less negative in the case of Wisprofloc-N. This suggests that under the investigated circumstances the bridging mechanism typical for anionic and non-ionic polyelectrolytes, had a minor effect as compared to that of the charge neutralization occurring in the case of the cationic polyelectrolytes. It is further suggested that the algae concentration in our model water was insufficient to allow for successful bridging to occur between algae. Anionic polyelectrolytes are adsorbed by particles through intervention of metal ions such as calcium. Under the model water circumstances it could be that the availability of calcium in the range of 150 mg CaCO₃/L enhanced adsorption and hence removal efficiency compared to the non-ionic Wisprofloc-N.

Cationic polyelectrolytes are suggested to be effective coagulant aids for algae laden water coagulation, and treatment by DAF. The charge and weight of the polyelectrolytes determine the process efficiency.

b. Polyelectrolytes as single coagulants

The application of polyelectrolytes as sole coagulants is not common in European water treatment, although it often leads to efficiency comparable to metal coagulants. This restriction is mainly due to health concerns. The most efficient polyelectrolyte as sole coagulant in this study was the cationic polyelectrolyte Superfloc C-573. The particle (alga) removal efficiency increased with the polyelectrolyte dose, the highest tested dose of 3 mg Superfloc C-573/L resulting in 81% removal efficiency (Fig. 4.7), which was higher than the maximum removal efficiency obtained by iron coagulant without coagulant aid under optimal coagulation and flocculation conditions.
(71%). The same holds for turbidity: the polyelectrolyte caused a removal efficiency of 74% as compared to 56% obtained by iron coagulant [3] (Fig. 4.8). Two mechanisms are suggested to be responsible for the polyelectrolytes efficiency: (i) improved coagulation of the algae, due to polyelectrolyte adsorption followed by charge neutralization, and (ii) improved attachment of the positively charged floc material to the negatively charged air bubbles [70]. The steep rise in the DAF removal efficiency obtained for the Superfloc C-573 polyelectrolyte suggests that a dose higher than 3 mg/L may have further increased efficiency.

![Particle removal efficiency (DAF) for different types and doses of polyelectrolyte as sole coagulant. Conditions: ≈10,000 cells/mL, initial turbidity 3.8 FTU, pH 8, G=30 s⁻¹, tₐ=10 min, R=7%, P=500 kPa.](image1)

**Fig. 4.7**

![Turbidity removal efficiency (DAF) for different types and doses of polyelectrolyte as sole coagulant. Conditions: ≈10,000 cells/mL, initial turbidity 3.8 FTU, pH 8, G=30 s⁻¹, tₐ=10 min, R=7%, P=500 kPa.](image2)

**Fig. 4.8**

Superfloc C-573 emerges as an attractive polyelectrolyte when used as a sole coagulant; this is further supported by the absence of carry-over of metal hydroxide flocs, lower amount of salts, and lower sludge volume. On the other hand, this sludge may be more difficult to dewater and dispose (environmental concerns). Furthermore, accurate determination of the residual is difficult, raising health concerns.
The second cationic polyelectrolyte Wisprofloc-P as a sole coagulant resulted in relatively high particle removal in the range of 75% (Fig. 4.7). However, turbidity removal was inferior, actually resulting in an increase of the original turbidity of the raw water in the case of the highest tested dose (Fig. 4.8). Characteristic for this polyelectrolyte is its high molecular weight (long polyelectrolyte chain structure), and weaker electric charge compared to Superfloc C-573. This resulted in the formation of comparatively voluminous and weaker flocs which tended to settle or stick to the glass surface of the jars and the mixing equipment. Destabilisation is suggested to have occurred as a combination of adsorption, as well as bridging mechanisms. The relatively weak charge density of the polyelectrolyte could be insufficient to promote a flat configuration on the alga surface, thus leaving its long polyelectrolyte chains protruding into the solution and bridging with other algae or negatively charged sites on existing flocs. EM measurements showed that Wisprofloc-P treatment was accompanied by only slight charge neutralization of the algae (Fig. 4.9).

![Graph showing electrophoretic mobility of particles for different types and doses of polyelectrolyte as sole coagulant](image)

**Fig. 4.9** Electrophoretic mobility of particles for different types and doses of polyelectrolyte as sole coagulant. Conditions: 10,000 cells/mL, pH 8, G=30 s⁻¹, t_r =10 min, R=7%, P=500 kPa.

Based on the particle removal efficiency, it is suggested that most of the existing algae were flocculated, however the character and quality of these flocs were inferior for efficient DAF. Furthermore, all the applied doses resulted in high residual turbidities presumably of polyelectrolyte origin. These observations suggest that the Wisprofloc-P polyelectrolyte is preferably applicable in cases where sufficient destabilisation has already been imposed e.g. by metal coagulants, in other words as a low-concentration coagulant aid. Similarly, it may be expected to be efficient when the concentration of the particulate and colloidal matter is relatively high, thus providing ample adsorption coagulation opportunity.

The bridging mechanism proved to be efficient in the case of the anionic polyelectrolyte Superfloc A-100 also, resulting in particle removal efficiency in the range of 75%, however, with low turbidity removal of 10-15% presumably ascribed to the residual polyelectrolyte. The presence of metal ions such as Ca²⁺ (raw water hardness of 150 mg/L expressed as CaCO₃) in the water provided good conditions for the occurrence of efficient particle coagulation and flocculation. The negative charge of the flocculated material obviously further increased with increase of the anionic
polyelectrolyte dose. This suggests that the particle removal in DAF occurred primarily as the result of particle-bubble interception, owed to the large bubble concentration relative to the particle (floc) concentration. The negative charge of the polyelectrolyte did not allow for its more complete incorporation into the floc matter. Furthermore, the negatively charged non-flocculated part of the polyelectrolyte was more difficult to remove by the negatively charged air bubbles. This resulted in inappropriate polyelectrolyte presence and coupled turbidity in the effluent.

Finally, the non-ionic polyelectrolyte Wisprofloc-N resulted in the poorest removal efficiency, both in terms of particle (algae) and turbidity removal. The bridging mechanism involved in the particle destabilisation in case of non-ionic polyelectrolytes occurs via hydrogen bonding and proved inefficient under the test circumstances. The particle charge (EM) showed a slight decrease of the original negative charge (Fig. 4.9). Flocculation occurs to some extent as visually observed, however inefficient and incomplete.

The relatively good model water quality, in which moderate concentrations of algae were the only significant contributor to the suspended matter, created conditions that were presumably not appropriate for the particle bridging coagulation by the anionic or non-ionic polyelectrolytes. Although generally recognized as more efficient, in particular for the removal of microorganisms such as algae, cationic polyelectrolytes are not a guarantee for efficient coagulation and downstream removal efficiency. Practical experience can allow to roughly predict the effect of a certain polyelectrolyte on the process efficiency. However, the optimal process efficiency and polyelectrolyte choice should be tested case by case. Under the tested circumstances, the application of the synthetic cationic polyelectrolyte Superfloc C-573 proved to be an effective and competitive coagulant at pH 8.

4.3.3 Ozone conditioning

Ozone conditioning of the algae resulted in significant DAF efficiency improvement. The results from one series of ozone conditioning experiments are presented in Fig. 4.10. The ozone dosing was based on similar research [47]. A range of low (0.2 mg O₃/mg C, or 0.48 O₃/L), medium (0.5 mg O₃/mg C, or 1.2 mg O₃/L) and high (0.9 mg O₃/mg C, or 2.16 mg O₃/L) ozone doses were tested in combination with the optimal iron coagulant dose of 3 mg Fe(III)/L, and with 1.5 mg Fe(III)/L and 4.5 mg Fe(III)/L. The results show that the low and medium ozone doses in combination with the 1.5 mg Fe(III)/L dose resulted in slightly deteriorated DAF efficiency, however, the combinations with the optimal (higher) iron dose resulted in all cases in significantly improved removal efficiency (80-97%), approaching 2 log particle removal for the high ozone dose. Full scale ozofloation (combined ozonation and DAF in one unit) of Thames Water at Walton Works (UK) with PAC (polyaluminum chloride) as coagulant, resulted in 20-88% chlorophyll reduction in case of 0.5 and 4 mg O₃/L respectively, compared to 20% achieved without ozone [71]. In the case of 4 mg O₃/L the down-stream algae filtration removal efficiency was 99%, compared to 55% without ozone application. Other ozofloation facilities in France achieved in 55-85% algae removal for an ozone dose of 1.6 mg O₃/L, the variation depending on the predominant algae species, the most abundant and difficult to remove being the blue-green Gomphosphaeria spp. [72]. Ozone induced flotation at very high doses of 15-50 mg O₃/L has been noted to reduce total suspended solids, including algae from a waste-water stabilization pond by 98% [73].
Fig. 4.10  Removal efficiency of particles, turbidity, and coagulant for different combinations of ozone and coagulant doses.

While DAF reduced algae by 1 log unit, intermediate ozone application after DAF reduced downstream filtrate algae concentration by 2-3 log units [74]. Pilot plant direct filtration efficiency of 1 log algae removal was raised to approximately 3 log removal after ozonation, providing also longer filter run-time [36].

In our case particle and turbidity removal efficiency increased with increase of the coagulant dose for each ozone dose, while the combinations of ozone and iron tended to be consistently more efficient in the case of the low and high ozone dose as compared to the medium one. This finding is related to the complicated chemistry of ozone and the induced release of EOM and possibly IOM, which is algae species and age specific [71, 72, 75]. The extent of the reaction of EOM and IOM with ozone depends on the dose. This phenomenon is further discussed in Section 4.3.3.a.

The results from the one way ANOVA for the case of 3 mg Fe(III)/L in combination with different ozone doses are summed-up in Fig. 4.11. The results suggest that ozone significantly affects the particle (alga) removal efficiency (P=0.00001) and not significantly the turbidity removal efficiency (P=0.48). The notation a, b and ab denote similarities between treatments based on multiple comparison analysis, suggesting that all ozone doses perform significantly better than the iron coagulant alone, however with no significant efficiency differences between themselves. One way ANOVA for the initial particle count shows that the initial conditions (with respect to particle - algae count) were significantly different for different ozone treatments (P=0.0047). However, including initial particle count as a covariate in the ANOVA still suggests that the particle removal efficiency is significantly affected by different ozone treatments. One way ANOVA for the initial turbidity shows that the initial conditions (with respect to turbidity) were not significantly different (P=0.12). Including the initial turbidity as a covariate in the ANOVA
suggests that ozone treatment had a significant effect on the turbidity removal efficiency.

![ANOVA results](image)

**Fig. 4.11** One way ANOVA for the combination of 3 mg Fe(III)/L iron coagulant and ozone treatment.

Multiple regression analysis for the initial particle count and ozone treatment (as independent variables) shows that they both significantly affected the particle removal efficiency (with ozone as a dependent variable $r^2=0.56$, $P=0.0015$; and with initial particle count $P=0.028$). Similar results were achieved by multiple regression analysis for turbidity and ozone treatment ($r^2=0.47$, $P=0.0018$ for ozone; and $P=0.00034$ for the initial turbidity).

In case of a higher coagulant dose of 5 mg Fe(III)/L the same conclusions were reached (Fig. 4.12). In order to assess the influence of the different coagulant dose in combination with ozone, a two way ANOVA was performed on the 3 mg and 5 mg Fe(III)/L cases. Although the results suggest a tendency of slightly increased DAF efficiency for the higher coagulant dose, especially with regard to particle removal (estimated 5%), no significant differences between treatment were found, both for particle count ($P=0.098$ for the coagulant dose, $P=0.85$ for the ozone dose, and $P=0.999$ for the combined influence of ozone and iron dose) and turbidity ($P=0.68$ for the coagulant dose, $P=0.80$ for the ozone dose and $P=0.70$ for the combined influence of ozone and iron dose). Two way ANOVAs for the initial particle count and the turbidity showed that the initial experimental conditions (in terms of both particle count and turbidity) were not significantly different. Multiple regression analysis for the particle removal efficiency ($r^2=0.57$) shows that it depended significantly on the ozone dose ($P=0.0011$) and the initial particle count ($P=0.017$), while it depended insignificantly on the iron coagulant dose ($P=0.082$). Multiple regression analysis for the turbidity removal efficiency ($r^2=0.2$) similarly shows that it was significantly affected by the ozone dose ($P=0.036$) and the initial turbidity ($P=0.013$), while it was insignificantly affected by the iron coagulant dose ($P=0.165$).
Fig. 4.12 Particle and turbidity removal efficiency for the combination of 5 mg Fe(III)/L iron coagulant and ozone treatment.

Experimental series with model water that contained a 50% lower initial algae concentration yielded similar efficiency results (Fig. 4.13).

Fig. 4.13 Removal efficiency of particles, turbidity and coagulant for different combinations of ozone and coagulant doses. Initial algae concentration = 5,000 cells/mL.
The same trend of low and high compared to medium ozone dose efficiency was observed again, however, ozone application resulted in a general low efficiency in combination with the low and medium coagulant dose. Although the combinations of ozone with high coagulant dose resulted in improved process efficiency compared to the zero-ozone case, ozone application in this case seemed to raise the coagulant demand. Based on comparison of these results and the results for the 10,000 cells/mL case, it can be argued that a critical dissolved organic matter concentration has to be present, and hence a minimal concentration of algae that are assumed to be the cause for a substantial part of such dissolved matter, in order to benefit from ozone conditioning [26, 45]. Higher initial particle concentration also provides more opportunity for the effectuation of the bridging mechanism which is directly related to: (i) collision frequency between the particles and (ii) the EOM secreted by the algae.

a. Mechanisms of ozone induced flocculation

Increased process efficiency by ozone has been attributed to ozone induced changes of pH or calcium precipitation during ozonation [76]. This implies that the same effects induced by ozonation could be induced by decreasing the pH with strong acids, or by carbon dioxide stripping and thus causing precipitation of supersaturated calcium carbonate. The pH of the water used for preparation of the model water was 7.9±0.2. Prior to the ozonation the pH was corrected to 7.5 by HCl addition. However, after ozonation the pH variation was 7.5 ± 0.2, suggesting that these arguments do not hold in this case.

Ozone conditioning can be regarded responsible for the creation of stress conditions in the algae environment, which results in the intensified excretion of EOM. The particle count of our ozonated model water (particle sized <10 μm) at a relatively low dose of 0.2 mg O₂/mg C (or 0.48 mg O₂/L) prior to further treatment, was decreased by 30%, while the concentration of particles larger than 10 μm increased (Fig. 4.14). This could be explained by algal cell lysis and IOM leakage that initiated spontaneous micro-flocculation. Among algae characteristics that have been suggested to affect process efficiency are the extra cellular and intra cellular organic matter (EOM and IOM). Their concentration, composition and characteristics (molecular weight) vary for different algae species [77], growth phase and growth conditions [78]. A substantial amount of the total
assimilated carbon can be released in the water in the form of EOM (up to 50%), while stress growth conditions (e.g. related to availability of light and nutrients) may increase this amount up to 95% [79]. Major EOM constituents have been analyzed for different species [80] and can generally be characterized as neutral and acidic polysaccharides and nonsaccharide acidic macromolecular compounds. Under certain water quality and coagulation conditions (DOC<3 mg/L, ratio between algogenic organic matter (DOC) and particle surface concentration <75 mg/m², and ferric salts used as coagulant at pH 6.5), the EOM, especially its neutral and acidic polysaccharides component, have been considered as anionic polymer coagulant aids. The EOM coagulant aid effect is asserted through: (i) attachment to particulate matter via ligand complexes, (ii) chemisorption and further coagulation of particles by the bridging mechanism, or (iii) by particle capture in a gel like structure. The model water DOC content was relatively low (<2 mg C/L). Furthermore, this water had been subjected to ozonation in a full-scale treatment process (3 mg O₃/L) before being abstracted and used in the experiments. So it can be expected that the initially present organic matter had already been substantially modified before spiking it with the algae. Therefore, the ozone that was added during the experiment reacted preferentially with the spiked algae and caused the release of EOM and IOM.

On the other hand, the significance of fine organic matter matrices or meshes of filaments which embed very small organic and inorganic colloids in the water, has been recognized as a very important determinant of their coagulation and sedimentation behaviour in natural surface water [81]. The higher molecular weight EOM constituents (>100,000 D) play a significant role in the formation of these organic matrices. Thus, the organic matrices which embed released EOM biopolymer, may facilitate the inter-particle bridging mechanism to a certain degree. On the other hand, excessive EOM release may hinder the flocculation process by coating of the particles and increasing their negative charge, as well as densening the organic matrice structure to an extent which makes particle-metal coagulant contact and flocculation more difficult.

The issue of possible algal cell lysis and release of IOM into the water still remains controversial [27, 43, 82]. This release depends primarily on the ozone dose, but also on the alga species and the presence of other natural organic matter (NOM) in the water, which may preferentially react with ozone. SEM analysis of ozonated algae spiked in untreated reservoir water (Fig. 4.15) and containing ozone scavengers, strongly suggests algal lysis and leakage of inner cell constituents occurring at an ozone dose of 0.57 mg O₃/mg C (or 2.0 mg O₃/L). Measurement of UV₂₅₄nm absorbance further support this. Although weakly correlated with the DOC concentration [27, 36], it may be a useful indicator of process efficiency. It is indicative of the presence of organic compounds which contain a hydrocarbon ring in their structure (e.g. aromatic and pigmented compounds). The verified algae cell lysis strongly implies the involvement of IOM, together with EOM, in the observed flocculation improvement.

The low, medium and high ozone doses (0.2, 0.5, 0.9 mg O₃/mg TOC) resulted in different DAF removal efficiency, both for the 10,000 cells/mL (Fig. 4.10) and the 5,000 cells/mL algae concentration. Although these differences were statistically not significant (Fig. 4.11), the low and the high ozone dose tended to perform better than the medium dose. In view of the previous discussion on the effect of ozone on the algae cell structure and EOM and IOM leakage (Fig. 4.14 and 4.15), and their effect on removal efficiency, UV₂₅₄nm absorbance of the water was measured for different ozone doses and times after ozonation (Fig. 4.16).
Fig. 4.15  Scanning electron microscopy (SEM) of *M. aeruginosa* spiked in reservoir water before and after ozonation at a dose of 0.57 mg O$_3$/mg C (2 mg O$_3$/L).
The low ozone dose (0.2 mg O₂/mg C) steadily increased the absorbance over in time, suggesting gradual release of algae EOM and IOM into the water. The medium ozone dose (0.5 mg O₂/mg C) caused a higher increase of the absorbance, suggesting a higher EOM and IOM content in the water. This dose resulted in modification of the released organic matter and a steady decrease of the absorbance with time. The 0.9 mg O₂/mg C and 1.3 mg O₂/mg C doses, both resulted in a decrease of the raw water absorbance, suggesting that the ozone concentration was high enough to not only cause the release of algae EOM and IOM, but also to substantially modify them through oxidation and reduction of their aromatic character.

![UV absorbance graph](image)

**Fig. 4.16**  \( \text{UV}_{254} \) absorbance in the water after ozone dosing, as a function of the ozone dose and time.

It has been reported that ozonation decreases the molecular weight of the present organic matter, which becomes more acidic and hydrophilic than the parent organic material [46], while the particle charge is reduced (Fig. 4.17).

![Electrophoretic mobility graph](image)

**Fig. 4.17**  Electrophoretic mobility (EM) of raw, ozonated and flocculated water as a function of ozone and coagulant dose.
The increased acidic functional group content is reported to provide for higher sorbability to metal-hydroxy species formed during the metal coagulant hydrolysis. This may result in the formation of more stable (i.e. of increased negative charge) particulate and colloidal material than before ozonation, which can impart an additional coagulant demand [6, 82]. This is observed in Fig. 4.10 for the high ozone dose of 0.9 mg O$_3$/mg C where the increase of the coagulant dose resulted in increased residual coagulant, suggesting the formation of difficult to remove soluble complexes of the modified organic matter and the added iron coagulant.

The higher the ozone dose, the larger the amount of released EOM, but also the larger the possibility of cell lysis and IOM release. Furthermore, the higher the ozone dose, the more significantly the NOM and EOM/IOM were modified by oxidation. While the low ozone dose seemed to cause moderate amounts of released EOM and IOM which benefitted flocculation, the medium dose resulted in EOM, but also in more substantial IOM release, which seemed to impair flocculation (Figs. 4.10 and 4.16). The high removal efficiency for the larger doses of ozone is suggested to be the result of larger EOM and IOM release, which however, is compensated by extensive reaction of the excess ozone with these compounds. Therefore, the application of low ozone doses in the range of 0.2 mg O$_3$/mg TOC was found most suitable for algae conditioning purposes under the bench-scale jar test conditions.

b. The effect of ozone on particle size distribution

Results (Fig. 4.18) suggest that ozone decreased the volume of small particles and increased the larger particle size fraction, which partly coincides with the particle counter results (Fig. 4.14).

![Particle size distribution graph](image)

Fig. 4.18 Particle volume distribution as a function of ozone dose (0.2 and 0.9 mg O$_3$/mg TOC).
The increase of the larger particle size volume fraction is not very obvious from the graph, since the impact of a larger particle on the volume distribution is much higher than that of a smaller size one. This suggests that: (i) cell lysis took place to a certain degree, and (ii) consequent spontaneous micro-floculation has been induced due to EOM and IOM. Cell lysis may have contributed to the rise of concentration of particles in the size range below the detection limit of the computer image analyser (1.9 μm), however, it is also likely that a portion of these is entrapped in the floc material which spontaneously formed due to EOM and IOM release. An increase of the overall particle volume has also been registered, suggesting the production of hydrophilic floc material with water entrapped within a hydrous floc structure. This is more pronounced in case of the lower ozone dose, presumably due to continued reactions with the organic matter of excess ozone in the case of the higher ozone dose. The influence of further coagulant addition and floculation, as well as the down-stream DAF, on the particle size and volume distribution depend on the process conditions.

The effect of ozone on the particle size distribution still remains controversial. Similar to our results, it has been stated that ozone application shifts the particle size distribution towards larger sizes, thus indicating the initiation of spontaneous microfloculation. In addition, ozone is known to induce the formation of colloidal matter from dissolved organic matter and it enhances its subsequent removal [26, 29, Section 4.3.3]. However, others stated that ozone did not have a significant effect on the particle size distribution, whilst resulting in an increase of the smaller size fractions [25, 83]. Ozonation has also been found to decrease the overall particle volume and mass and result in lower filter loading [84]. These effects of ozone, however, appear to depend on the ozone dose and may result in contradictory findings; higher doses tend to be associated with reduction of the amount of particles in the larger size range, and with lower particle volume and mass [85].

One of the probable reasons for the inconsistencies is the use of non-standardised observation equipment (different types of light-blocking or laser particle counters, image analysis systems, etc.) which often have a limited applicability. One such limitation is related e.g. to the use of the (light-blockage) particle counter in this research. The high shear forces which are applied during the passage of the sample through the orifice of the counting cell may cause break-up of aggregates, which makes it a less reliable qualitative assessment method of flocculated and ozonated water. In view of the limitations of the available particle counting techniques we applied the Mini-Magiscan (IAS 25/TV25 Joyce-Loebl Ltd., UK) computer image analysis system, which proved to be especially useful for the characterisation of ozonated and flocculated water. It provides minimum sample disturbance and may be regarded as more reliable for such purposes.

c. Combined ozone and polyelectrolyte treatment (alone or combined with metal coagulant)

The combination of ozone and polyelectrolyte treatment has been assessed before, especially for cationic polyelectrolytes [34, 43, 84]. Process efficiency was expected to improve due to the effects of the ozone-induced biopolymers and the cationic polyelectrolyte charge. The positive effect of the latter is assumed to be related to the reduction of the negative surface charge of the algae and the improvement of the particle collision kinetics. The cationic polyelectrolyte Superfloc C-573 and Wisprofloc-P were tested as sole coagulants and as coagulant aids in combination with ozone conditioning.
The efficiency of the Superfloc C-573 polyelectrolyte as a sole coagulant proved here to depend on the ozone dose (0.2 and 0.9 mg O₃/mg C, or 0.5 and 2.25 mg O₃/L) (Fig. 4.19, F and G).

Fig. 4.19  Removal efficiency for the combination of ozone dose conditioning with polyelectrolyte Superfloc C-573 as coagulant aid or as sole coagulant.

The process efficiency for the same polyelectrolyte dose (1.0 mg C-573/L) was lower for the high ozone dose (0.9 mg O₃/mg C) than for the low one (0.2 mg O₃/mg C), especially regarding the particle removal. Considering the relatively clean model water circumstances in which the coagulant demand was exerted mainly by the organic matter, the increase of the ozone dose results in changes in the NOM structure which eventually result in lower MW and more acidic and hydrophilic compounds. The influence of these changes on coagulant demand depends on their extent. In case of metal coagulant application the increased acidity tends to increase the affinity of the organics to the metal hydroxide, thus increasing metal coagulant demand, while the MW decrease tends to produce the opposite effect. The same applies for polyelectrolyte coagulants, since most of them selectively precipitate high MW and NOM with low functional group content. Ozonation causes the opposite effect [6, 83]: ozone decreases the particle surface charge, thus decreasing the amount of polymer needed to neutralize it and theoretically decreasing the polymer demand. However, the amount of precipitated TOC under such conditions decreases due to the preference of the polymers for organics with high MW and low functional group content.

Thus, the high ozone dose is suggested to disfavour particle flocculation through the applied polymer coagulant and to have resulted in lower DAF efficiency. The high ozone dose reduced the initial particle (alga) count by 25%, reflecting algal lysis and EOM and IOM leakage. Under these conditions, the particle (alga) count after DAF remained at the same level reached after ozonation, suggesting that the EOM and IOM interfered with the coagulation (the algae were not properly destabilised and flocculated) and that the polyelectrolyte was ineffectively utilised. It is also suggested that ozone and its hydroxyl radical may oxidise some of the polyelectrolyte
molecules resulting in inefficient particle coagulation; this is more pronounced for the higher ozone dose. In the case of the low ozone dose the initial algae count was reduced by only 7%, suggesting only minor IOM leakage accompanying the EOM release and probably less changes in their original structure. These conditions (Fig. 4.19, F) resulted in more efficient coagulation and flocculation of the algae and in higher particle and turbidity removal than the ozone + metal coagulant combination (Fig. 4.19, B and C). In both cases this was accompanied by a decrease of the UV<sub>254</sub> nm absorbance; the DOC content was more substantially reduced in the case of the lower ozone dose.

In the case where polyelectrolyte was used as coagulant aid (D and E), the overall NOM removal efficiency has been suggested to depend on the concentration ratio of metal coagulant to polyelectrolyte [6, 83]. The overall effect of the ozonation on the coagulation in the case of dual coagulants (metal coagulant + polyelectrolyte) depends on the individual characteristics of each coagulant.

The results show that the characteristics of the polyelectrolyte play a specific role (Fig. 4.20). Ozonation in the case of a medium Superfloc C-573 polyelectrolyte coagulant aid dose range (D and E; 0.3 and 0.5 mg C-573/L) tended to perform slightly better than the metal coagulant only (A), even when the coagulant dose was doubled (B). Unlike the case where the same polyelectrolyte was applied as a sole coagulant, the DAF efficiency tended to improve with an increase of the ozone dose (data not presented here), suggesting that in this case the cationic polyelectrolyte induced adsorption phenomena compound the conditioning effect of the ozone and particle destabilisation by the metal coagulant. This discussion is supported by EM measurements, with the particle surface charge decreasing with the polyelectrolyte dose. Although the Wisprofloc-P polyelectrolyte proved beneficial for the flocculation and DAF removal of the algae in the ozone + Fe(III) coagulant scheme, its weaker charge density and resultant high residuals are suggested responsible for the accompanying high residual turbidities (F, G and H).

![Graph](image)

**Fig. 4.20** Removal efficiency as a function of low ozone dose conditioning in combination with cationic polyelectrolyte Superfloc C-573 and Wisprofloc-P coagulant aid.
Fig. 4.21 shows the results from the two way ANOVA for iron coagulant alone, the combination of iron and Superfloc C-573 as coagulant aid, the combination of ozone conditioning and iron coagulant, and ozone conditioning, iron coagulant and Superfloc C-573 coagulant aid.

The particle removal efficiency is statistically significantly affected by ozone, Superfloc C-573 coagulant aid, and by the combination of both. The turbidity removal efficiency, on the other hand is not significantly affected by these parameters, however, introducing the initial turbidity in the ANOVA as a covariate suggests that turbidity removal was significantly affected by the polyelectrolyte and the combination of polyelectrolyte and ozone, but not by ozone alone ($P=0.32$ for $O_3$, $P=0.002$ for polyelectrolyte and $P=0.049$ for the combination of polyelectrolyte and ozone). Two way ANOVA for the initial turbidity and particle count showed that the initial turbidity was not significantly different, but that initial particle count was significantly different for the different experiments. Multiple comparison analysis shows that for particle removal efficiency there is a significant difference between the iron coagulant treatment only (Fig. 4.21; 1) and the other treatment options (2, 3 and 4), however, the results for the latter did not significantly differ from each other. Similarly, if initial particle count is included in the analysis as a covariate, the results for the iron coagulant only and the other treatment options were again significantly different ($P<0.001$). The multiple comparison analysis for turbidity removal efficiency showed that there was no significant difference between the different treatment options 1 to 4, however, introducing the initial turbidity as a covariate in the analysis suggests again that polyelectrolyte and the polyelectrolyte + ozone conditioning significantly affect the DAF removal efficiency. Multiple regression analysis for the particle removal efficiency (as the dependent variable, $r^2=0.69$) showed that the application of ozone ($P=0.04$) and polyelectrolyte ($P=0.00036$) significantly affected it, while the initial particle count ($P=0.58$) did not. Multiple regression analysis for the turbidity removal efficiency (as the dependent variable, $r^2=0.35$) showed that the polyelectrolyte ($P=0.0025$) and the initial turbidity ($P=0.011$) significantly
affected it, while the ozone \( (P=0.14) \) did not.

The influence of the ozone dose on the process efficiency proved to be larger in the case of application of cationic polyelectrolytes as sole coagulants compared to the case when it was used as a coagulant aid to Fe(III) coagulant. This implies that process flexibility is lower and that if this option would be applied in practice the process would need to be optimised more frequently. Dual coagulant systems provided more flexibility in this sense, as the polyelectrolyte had a synergistic effect on particle destabilisation, to that of the metal coagulant. Optimisation of the polyelectrolyte coagulant aid dose is likely to lower required coagulant doses. The positive effects of polyelectrolyte application in this case, such as reduced coagulant demand and lower filter headloss, must be balanced with the possible negative effects, e.g. higher polyelectrolyte residuals and accompanying turbidity, and higher organic matter, presumably AOC, in the effluent.

d. Point of coagulant addition

The point of coagulant addition relative to the ozone can influence process efficiency. Our experiments with a low dose of ozone (0.2 mg O\(_3\)/mg C or 0.48 mg O\(_3\)/L, with 3 mg Fe(III)/L) showed that increase of the time lag between the ozonation and the coagulation from 1.5 to 9 min, slightly increased DAF removal efficiency (Fig. 4.22). This is contrary to previous results from research on the application of ozone as an algae conditioner in the context of direct filtration [36]. There, an increase of the time lapse between ozonation and coagulant addition from 1-10 min was found to negatively influence process efficiency.

![Graph showing DAF removal efficiency as a function of the time gap between ozonation and coagulation.](image)

**Fig. 4.22** DAF removal efficiency as a function of the time gap between ozonation and coagulation.
In both cases similar ozone doses were used, however, in the direct filtration case raw Biesbosch Reservoirs water had been used for the experiments [36], while in our case the model water was prepared by using Biesbosch Reservoirs water after it had already been treated with ozone in the full-scale treatment. This implies that the organic matter present before treatment had already been oxidised and modified. Our model water was thus, characterised by very small particulate matter concentration except for the spiked algae, while the largest portion of the TOC was DOC (80%>DOC>85%). In such circumstances, the spiked algae were presumably the only significant source of particulate and dissolved organic matter which was prone to react with the newly applied ozone, and affect the process efficiency.

The observed differences between our results and that of others [36], can partly be explained with the raw water quality differences. In our case, the removal efficiency for the shortest time lag of 1.5 min was already high (>90%), suggesting very fast reactions of the ozone with the algae within this time after ozone application. In both cases the mg CaCO₃/mg TOC ratio was 60-70, which favours ozone effects on flocculation [47]. At this ratio and the used ozone doses, the efficiency rose with the elapsed time before coagulant addition, suggesting that ozone continued to react with the algae. The applied ozone dose was probably not high enough to further extend organic matter changes and increase coagulant demand, which is in accordance with other findings [84]. Although not tested in this experiment, the application of a higher ozone dose (e.g. in the range of 1.0 mg O₃/mg C) may produce a different effect, in which the additional ozone is likely to further oxidise the organic molecules into compounds with a MW and acidic functional group content that may impart an additional coagulant demand.

4.3.4 KMnO₄ conditioning

Till now the use of potassium permanganate for algae conditioning in the context of DAF hasn’t been considered. The benefits which arise from its application include taste and odour removal, a bactericidal effect, the reduction of the THM formation potential and the absence of potentially harmful by-products.

KMnO₄ dose optimisation for a constant iron coagulant dose in model water (Fig. 4.23) shows that an optimal dose of 0.7 mg KMnO₄/L more than doubled the DAF particle removal efficiency achieved with the iron coagulant only. However, the accompanying turbidity removal was not much affected, presumably due to the high residual Mn values (Fig. 4.24). The optimal permanganate dose coincided with the visually determined permanganate demand (no pink colour observable after DAF). Excessive permanganate dosing caused colouration of the water and lowering of the process efficiency. The influence of an increase of the permanganate dose on the residual Mn fractions is seen in Fig. 4.24. Both, the residual dissolved MnO₄⁻ and colloidal MnO₂ concentrations increased with the permanganate dose, which is in accordance with reports by Middlemans and Ficek [49].

For the same KMnO₄ dose the permanganate (dissolved Mn) decreased non-linearly with time (Fig. 4.25). 60% of the overall KMnO₄ reduction which takes place within the 30 min available contact time before coagulation, occurred during the first 5 min. The precipitation rate of colloidal MnO₂ for the 0.7 mg KMnO₄ dose and the model water conditions was 0.135 mg Mn/L, or 0.214 mg MnO₂/L in the 30 minutes of contact time. Fig 4.25 suggests that although the KMnO₄ contact
time in the experiments was rather long, the results from the KMnO₄ conditioning experiments would be valid for contact times as short as 20 or even 15 minutes, because very little permanganate reduction took place after the 15 min.

![Graph showing removal efficiency of particles and turbidity against KMnO₄ dose](image)

**Fig. 4.23** Optimisation of the KMnO₄ dose for a constant dose of coagulant (5 mg Fe(III)/L), based on removal of particles and turbidity. Conditions: KMnO₄ contact time 30 min, contact and coagulation pH 8, G=70 s⁻¹, tᵣ=15 min, R=7%, P=500 kPa.

![Graph showing Mn residual against KMnO₄ dose](image)

**Fig. 4.24** Residual Mn concentration as a function of the KMnO₄ dose. Conditions: KMnO₄ contact time 30 min, 5 mg Fe(III)/L, pH 8, G=70 s⁻¹, tᵣ=15 min, R=7%, P=500 kPa.
Fig. 4.25  
KMnO₄ reduction for model water (≈10,000 cells M. aeruginosa/mL, pH 8), as a function of contact time.

The decrease of the permanganate concentration (dissolved Mn) after DAF was linear with increase of the conditioning (and coagulation) pH (Fig. 4.26), due to increase of permanganate reactivity with increase of pH.

Fig 4.26  
Total and dissolved residual Mn as a function of KMnO₄ conditioning and coagulation pH. Conditions: 0.7 mg KMnO₄/L, G=70 s⁻¹, t=15 min, R=7%, P=500 kPa.
Fig. 4.26 suggests that the accompanying high particle removal efficiency achieved at coagulation pH 6 conditions is to be ascribed predominantly to adsorption coagulation and charge neutralisation. These mechanisms are typical for such pH conditions below the IEP [3, 11, 12], compared to sweep coagulation occurring at the pH 7, 8 and 9 [86]. The high(er) permanganate concentration at pH 6 suggest that the permanganate reduction at this pH was substantially lower than at pH 7, 8 and 9. This again implies that at pH 6 less oxidative reactions with the algae and EOM took place, consequently less MnO₂ was produced and hence, lower flocculation rates should occur. At pH 6 one would expect efficient removal of the negatively charged MnO₂ by adsorption coagulation with the predominantly positively charged iron-hydroxo species [9, 10]. However, the principal mechanisms in which metal species and organic ions are adsorbed, are cation sorption and direct ion attraction. The cation exchange properties of MnO₂ are related to the functional groups at its surface, which strongly depend on pH [50, 60]. Thus, as a decrease of pH would result in a decrease of its negative charge and of its cation exchange capacity, this would result in lower adsorption of positively charged iron-hydroxo species onto MnO₂.

DAF efficiency is closely related to the applied energy input (G value) and flocculation time (t). In the case of permanganate conditioning, the removal efficiency of the residual colloidal MnO₂ forms an additional criterion of optimal flocculation. For our model water a Gt value of approximately 60,000 (G=70 s⁻¹ and t=15 min) was found appropriate for efficient and economical flocculation preceding DAF (Fig. 4.27).

![Graph showing particle removal efficiency as a function of Gt (and G); model water with KMnO₄ conditioning.](image)

This is in accordance to findings for algae laden water treatment by DAF [66] and practically applied Gt values [87] without KMnO₄ conditioning, although much lower Gt values (15,000-16,000) have also been implicated as favourable [65]. Prolonged flocculation times did not substantially increase process efficiency. Higher G values are suggested to have resulted in floc break-up, while lower ones did not provide sufficient contact opportunities per unit of time for efficient flocculation. In all tested cases discussed previously, the total residual Fe coagulant and
Mn concentrations were higher than their respective maximum allowable concentration (MAC) of 200 and 50 µg/L. Further process optimisation or modification may be required, as well as down-stream filtration.

a. Mechanisms of KMnO₄ induced flocculation

The results from the one way ANOVA (Fig. 4.28) for different treatment options including iron coagulant alone, combined KMnO₄ conditioning and iron coagulant, and combined KMnO₄ conditioning, iron coagulant and polyelectrolyte Superfloc C-573 coagulant aid, suggest that the particle removal efficiency was significantly affected by the different treatments. The same applies for the turbidity. Multiple comparison analysis for the particle removal efficiency suggests that the option including the polyelectrolyte (Fig. 4.28; 3) performed statistically significantly better than the other two treatment options (Fig. 4.28; 1 and 2). The same holds for turbidity. Although the KMnO₄ conditioning tended to raise the DAF efficiency where the iron coagulant was used, the obtained improvement was statistically insignificant. The standard deviation of the removal efficiency obtained with experiments was comparatively high (Fig. 4.28).

![Box plot of particle and turbidity removal efficiency](image)

**Fig. 4.28** Results from the ANOVA for different treatment combinations including KMnO₄ conditioning and combined KMnO₄ and polyelectrolyte treatment.

Although the algal concentration was kept constant, periodically a different permanganate demand was exerted, indicating that the organic matter content of the water nevertheless was varying. The TOC/DOC content of an algae batch was shown to vary at different growth stages, as well as different time after the algae were sampled from the original culture. Our attempts to correlate the DOC concentration with the achieved process efficiency proved not fully successful. This suggested that the DOC composition was a factor that affected the process efficiency as well. In the absence of significant amounts of other organic matter in the water, the spiked algae with their EOM and possibly IOM were the only significant contributor to the particulate and dissolved organic matter susceptible to KMnO₄ oxidation. The effect of the algal growth stage on the EOM
content composition and structure, and on flocculation process efficiency, is well documented [77, 78, 82, 85]. On the other hand, the longer the time gap between the algae sampling from the original culture and their actual addition to the model water, the higher the possibility of change of the quantity and composition of EOM. Although no characterisation (e.g. measurements of the MW) of the present EOM fractions for different experiments was done, this is suggested as one of the major sources of noted results inconsistency.

The overall effect of permanganate conditioning consists of its oxidative activity, and the flocculation and adsorption characteristics of the colloidal MnO\textsubscript{2}. Similar to ozone, permanganate application to algae laden water causes stress for the algae resulting in algal EOM release, which may serve as biopolymer [36]. The 0.7 mg KMnO\textsubscript{4} dose caused a 10% reduction of particle count suggesting IOM leakage as well. DOC and UV\textsubscript{254nm} increased by 6% and 65% respectively. Furthermore, the permanganate has been known to oxidise organic matter which may otherwise bind the iron and form soluble complexes, imparting an additional coagulant demand. It has also been suggested that the released biopolymer may initiate microfloculation even before coagulant addition [36]. In surface water rich in NOM fine organic matter matrices or meshes of filaments exist [81], both EOM and MnO\textsubscript{2} precipitates can be captured within the meshes, thus enhancing a bridging flocculation mechanism. The precipitated MnO\textsubscript{2} increases the overall particle concentration and adsorbs multivalent cations such as Ca\textsuperscript{2+}, organic molecules, and can be adsorbed on alga cells [36]. Although of high density (5,026 kg/m\textsuperscript{3}), the hydrous colloidal nature of MnO\textsubscript{2} provides conditions which do not necessarily favour settling of the algae. The MnO\textsubscript{2} adsorption on algae cells was accompanied by a slightly higher negative charge of the algae, as verified by EM measurements. The physical coverage of the algae by MnO\textsubscript{2} and the resulting increased negative charge contradict the requirements for their efficient flocculation. Yet, this effect could be balanced by the oxidising effect of the permanganate and the release of biopolymer which can behave as a coagulant aid. This leads to an overall better coagulation and flocculation of particles.

b. Combined KMnO\textsubscript{4} and polyelectrolyte treatment

The residual Mn after KMnO\textsubscript{4} conditioning and DAF was systematically higher than the 50 µg/l MAC. The negative surface charge of the colloidal MnO\textsubscript{2} at the tested pH 8, suggests the use of cationic polyelectrolytes can assist in its destabilisation and removal. The Superfloc C-573 and Wisprofloc-P polyelectrolytes were tested for the purpose. They proved efficient as coagulant aids to Fe(III) coagulant in a DAF scheme (Fig. 4.29), supporting the predominant sweep coagulation (see Chapter 3) by the neutralisation of the surface charge of MnO\textsubscript{2}. The results from the one way ANOVA (Fig. 4.28) suggested that although the KMnO\textsubscript{4} conditioning tended to raise the DAF efficiency where the iron coagulant was used, the only statistically significant improvement was obtained if cationic polyelectrolyte was introduced in the scheme.

As discussed in Section 4.3.5, the efficiency improvement achieved by the combined Fe(III) coagulant and polyelectrolyte treatment, especially in the case of the higher charged Superfloc C-573, was significant (Fig. 4.20). The incorporation of KMnO\textsubscript{4} conditioning in the scheme tended to raise the process efficiency further. This is valid in particular for the turbidity removal efficiency which improved by approximately 10-20%, although the introduction of the permanganate in effect increases particle concentration due to resulting MnO\textsubscript{2} production.
Fig. 4.29  KMnO₄ conditioning in combination with iron and cationic polyelectrolytes as coagulant aid.

Residual coagulant and manganese levels confirm that the lower final turbidity in the case of the KMnO₄-coagulant-polyelectrolyte scheme is caused by improved coagulant removal (Fig. 4.30).

Fig. 4.30  Residual Fe and Mn after DAF with different treatment combinations of KMnO₄ conditioning, Fe(III)coagulant and Superfloc C-573 polyelectrolyte treatment. Conditions: pH 8, G=70 s⁻¹, tₕ=15 min, R=7%, P=500 kPa.
Permanganate is assumed to react with the organic matter preventing it from complexing the iron coagulant into stable organo-iron compounds. This oxidative action ensures more complete coagulant utilisation for particle destabilisation. In this case it eventually resulted in better coagulant removal due to adsorption effects related to the cationic polyelectrolyte. The same adsorption coagulation effects are responsible for the reduction of the residual Mn below the 100 µg/L, suggesting that cationic polyelectrolytes may also be utilised successfully for the purpose of reducing the residual Mn. There were no indications that the applied KMnO₄ dose of 0.7 mg/L affected the polymer structure and its efficiency.

c. The effect of KMnO₄ on particle size distribution

Fig. 4.31 represents the particle volume distribution after KMnO₄ conditioning with a 0.7 mg/L dose and after different contact time.

![Particle size distribution graph](image)

Fig. 4.31 Effect of a 0.7 mg KMnO₄/L dose and contact time on the particle volume distribution.

The stress which results from the permanganate conditioning results in the excretion of algal EOM, as well as cell lysis and IOM leakage. Even at very short contact time of 1 minute there is a noticeable reduction of the volume of the smaller-size particles (predominantly algae) and an increase of volume of the larger-size particles. This indicates that spontaneous micro-flocculation was initiated by the EOM and IOM. Longer contact times did not have a more pronounced effect on the algal volume fractions, however, the larger-size particles were further modified resulting in more voluminous floc material with longer contact time. The particle distribution measurement did not allow to detect particles smaller than approximately 2 µm, which would encompass the colloidal (0.3-0.4 µm) MnO₂. As more permanganate will be reduced with time (Fig. 4.25), the MnO₂ and the submicron particle concentration will increase. The increase with its concomitant high adsorptive capacity principally results in an increase of the overall process efficiency. The MnO₂ fraction will be removed in the final filter, resulting in acceptable effluent Mn concentrations [22].
d. Reduction of KMnO₄ residual by Na₂SO₃

Chemical reduction of the permanganate Mn residual by Na₂SO₃ has been attempted with limited success in direct filtration [36]. The background motive for this approach was to reduce the dissolved permanganate Mn (VII) and simultaneously convert it into colloidal Mn(IV)O₂, which can be removed by the final filtration. The experiments here (at 0.35 and 0.7 mg Na₂SO₃/L) lowered total Mn, after DAF and prior to filtration, to levels in the range of 70 µg/l. These concentrations are low for the purpose. The stoichiometric amount of Na₂SO₃ necessary for the reduction of 1 mg KMnO₄/L is approximately 1.2 mg Na₂SO₃/L; a considerable time is needed to achieve complete reduction. Since flotation time is 15-30 minutes, full reduction by Na₂SO₃ may not be completed within the available flotation time. Increasing the dose of Na₂SO₃ in excess to the stoichiometric amount necessary for the reduction of the residual permanganate can speed up the permanganate reduction.

Finally, the chemical reducing activity of the down-stream filter should also be considered as a contributor to lower permanganate concentrations in the effluent.

4.4 CONCLUSIONS

Coagulant dose stoichiometry was established for single cell cyanobacteria Microcystis aeruginosa in the concentration range of 5,000-20,000 cells/mL. A further 25% rise of algae concentration did not raise the coagulant dose requirement, suggesting that a critical concentration of algae and of coagulant dose had been reached allowing for full utilisation of the sweep coagulation of the particles. This is supported by the fact that even the highest tested coagulant dose of 15 mg Fe(III)/L did not result in algae charge neutralisation, although particle charge neutralisation and charge reversal took place for the same dose in the absence of algae. It can be assumed that the IEP of the colloids in the absence of algae was shifted towards the neutral coagulation pH, resulting in particle charge reversal. The presence of the algae (and the constituents of their culture medium), prevented the IEP shift towards the neutral pH region and their charge neutralisation.

Polyelectrolyte as coagulant aid is a treatment process option which proved to be efficient in particle destabilisation. The efficiency for the two cationic polyelectrolytes (Wisprofloc-P and especially Superfloc C-573) was significantly higher than that of the metal coagulant alone under sweep coagulation conditions. A combination of 3 mg Fe(III)/L and 0.3 mg Superfloc C-573/L achieved 87% particles (algae) removal, compared to 84 % achieved with 3 mg Fe/L + 0.1 mg Wisprofloc-P, and 47% achieved by the 3 mg Fe/L only. The turbidity removal for these treatment options was 79%, 61% and 35% respectively. Both polyelectrolytes induced adsorption coagulation which supported the sweep coagulation; this was verified by EM measurements. The efficiency of the Superfloc C-573 and Wisprofloc-P depends on their electric charge and molecular weight characteristics. The more highly charged Superfloc C-573 proved to be more efficient and reliable than the ‘heavier’ but lower charged Wisprofloc-P, both in terms of algae and turbidity removal. The latter tended to form sticky floc material that kept being attached to any available surfaces. The bridging mechanism was prevalent in the case of the non-ionic and anionic polyelectrolytes; it proved to be of inferior efficiency as compared to the cationic polyelectrolytes’ charge neutralisation mechanism. The abundant presence of Ca²⁺ in the model water which
enhanced the adsorption of the anionic polyelectrolyte Superfloc A-100 onto the particles, is thought to be the reason for its slightly higher efficiency as compared to the non-ionic polyelectrolyte Wisprofloc-N.

**Polyelectrolyte as sole coagulant** is a treatment option which may result in similar (or slightly higher) DAF particle removal efficiency as compared to that of sole metal coagulants. This applies to cationic polyelectrolytes where particle adsorption, and in the case of Superfloc C-573 charge neutralisation, were again more efficient than the bridging mechanism associated with the non-ionic and anionic polyelectrolytes. The most important prerequisite for high particle and turbidity removal is the charge characteristic of the polyelectrolyte, which has an influence on the resulting floc size and structure. Polyelectrolyte doses >0.5 mg/L of the higher charged Superfloc C-573 resulted in smaller and more compact floc material compared to the same doses of the Wisprofloc-P polyelectrolyte, which again tended to produce large and sticky floc material. Hence, the difference in achieved DAF maximum particle and turbidity removal efficiency, which amounted to 81% and 77% particle removal for 3 mg Superfloc C-573 and 0.5 mg Wisprofloc-P, coupled to turbidity removal efficiency of 74% for the first, and only 12% for the second polyelectrolyte. The additional benefit of cationic polyelectrolytes application in the case of DAF is the increase of particle-bubble adsorption due to attraction forces between the negatively charged air bubbles and positively charged floc material.

The final choice of polyelectrolyte, whether as a coagulant or coagulant aid, also depends on the raw water characteristics, including the suspended and colloidal particles concentration, the TOC/DOC content and composition, the presence of ions such as calcium, etc. The cationic polyelectrolytes were overall more efficient and reliable in the context of DAF. However, the decision to apply them and the final type selection will also depend on the residual concentration after the final filter. The long-term health hazard related to consumption of water with polyelectrolyte residual, and the absence of real-time analytical technique calls for a careful approach.

**Ozone conditioning** is a pre-treatment option which proved efficient for improving the coagulation and flocculation before down-stream DAF. With the prerequisite that a range of raw water characteristics and process parameters can be addressed (e.g. 0.4-0.8 mg O₂/mg C, hardness to TOC ratio >25 mg CaCO₃/mg TOC, low bromide concentration, ozonation pH preferably <7.5 or even 7), the application of ozone may be considered a viable option for significantly increasing DAF efficiency. Ozone conditioning, initial particle count and initial turbidity were found to statistically significantly affect DAF efficiency. The resultant DAF particle and turbidity removal efficiency for different ozone doses (0.2, 0.5 and 0.9 mg O₂/mg C) did not significantly vary. The particle removal for these ozone doses combined with 3 mg Fe/L amounted to 91%, 89% and 90.5%, coupled to 50%, 52% and 56% turbidity removal respectively. However, the higher the ozone dose, the more significantly the organic matter (mostly algae, EOM and IOM) was modified, as measured by UV₂₅₄nm absorbance. An increase of the coagulant dose in combination with the same ozone dose did not improve DAF efficiency significantly, although a positive trend was noted. A coagulant dose of 5 mg Fe/L combined with the 0.2, 0.5 and 0.9 mg O₂/mg C doses, resulted in 96%, 94% and 96% particle removal, and 54%, 65% and 51% turbidity removal efficiency.

The principal mechanisms involved in the ozone induced flocculation effects are related to its
strong oxidising activity. Low ozone dosages of 0.2 mg O₂/mg C (or 0.48 mg O₂/L) reduced the initial particle count, indicating reaction with the ozone and modification of the algal cell wall layer, as well as partial rupture and lysis of the algae. Ozone application may be regarded as stress conditions for the algae, causing EOM release and possibly IOM leakage in the case of ruptured alga cells. This was verified by SEM observation, as well as by UV₂₅₄nm absorbance measurement, which is sensitive to the presence of dissolved organic matter with hydrocarbon rings in its structure, such as the pigmented compounds originating from lysed algae cells. The released EOM and IOM act as natural coagulant aid (biopolymer) and enhance flocculation; they may cause spontaneous micro-flocculation as verified by particle count and computer image analysis data. The micro-flocculation was stimulated by the ozone induced decrease of the initial algal surface charge and corresponding mutual electrostatic repulsion.

Larger doses of ozone (0.5 mg O₂/mg C) provided an opportunity for more pronounced oxidation and modification of the algae cells, resulting in further decrease of their initial concentration. This was accompanied by prolonged ozone activity, and the chemical modification of the EOM and IOM into compounds of lower MW and higher acidic group content, more hydrophilic organic matter compounds, and a resulting overall negative influence on the flocculation and the DAF efficiency. The highest ozone dose (0.9 mg O₂/mg C) had a severe impact on the algae population in terms of their EOM and IOM. The ozone further oxidized and split the released EOM and IOM compounds into ones with lower MW, which resulted in the formation of difficult to remove organo-iron complexes and increased residual coagulant in the effluent.

A similar tendency of slightly lower efficiency (compared to the lower and the higher ozone dose) was found to occur at a medium dose for a two times lower initial algae concentration. In this case the ozone appeared to induce an increase of the coagulant demand compared to the optimal dose for the coagulant without conditioning. This suggests that a minimum organic matter content has to be present in order to benefit from ozone conditioning. In the model water the main portion of organic matter prone to oxidative modification, was in the form of algae and their EOM and IOM. In the case of the higher algae concentration this resulted in improved flocculation through the enhancement of bridging flocculation. In reservoir water with often considerable amounts of colloidal and particulate inorganic and organic matter, the ozone conditioning may have different outcomes per location.

The use of polyelectrolytes as sole coagulant combined with ozone conditioning proved to be a relatively attractive option in view of the possible achievement of relatively high algae removal efficiency together with the absence of problems related to the complexing of metal coagulants by dissolved organic matter. This option mainly pertains to cationic polyelectrolytes and its efficiency is related to charge reduction effects. A combined 0.2 mg O₂/mg C and 1.0 mg Superfloc C-573/L treatment resulted in 86% particle removal and 75% turbidity removal. Although there was a slightly lower particle removal efficiency compared to the ozone + Fe(III) coagulant combinations, there was an improvement of the turbidity removal by more than 20%. This is related to the absence of the residual Fe coagulant in the effluent.

The cationic polyelectrolytes destabilise the ozone conditioned algae, which have a lower negative charge, by adsorption coagulation and partial charge neutralisation. The non-ionic and anionic character of the ozone induced EOM and IOM results in their adsorption onto the polyelectrolyte-floc material, resulting in overall good flocculation conditions. However, this option proved
sensitive to ozone overdosing, which resulted in deteriorated effluent quality. It is suggested that high ozone doses may not only affect the algal structure and result in higher amounts of, and more extensively oxidised EOM and IOM, but they may also oxidise some of the polyelectrolyte molecules, thus affecting the polyelectrolyte structure and lowering its efficiency.

**The use of polyelectrolytes as coagulant aid combined with ozone conditioning** tended to further increase the ozone-metal coagulant scheme efficiency, in the case of cationic polyelectrolytes. The combination of 0.2 mg O₃/mg C, 2.5 mg Fe/L coagulant, and 0.2 mg Superfloc C-573/L resulted in 95% particle removal and 59% turbidity removal, compared to a similar case in which a 0.1 mg Wisprofloc-P coagulant aid resulted in 99% particle removal, but very low turbidity removal of 14%.

The efficiency of (cationic) polyelectrolytes in this cases is based on aiding the particle flocculation by adsorption coagulation and charge neutralisation of particles which had already been destabilised by the ozone conditioning and the metal coagulant induced sweep coagulation. Consequently, the algae coagulation does not solely depend on the polyelectrolyte as in the previously discussed option, but instead the flocculation of already destabilised particulate matter is being aided by the cationic polyelectrolyte. Thus, more flexibility and reliability is provided for achieving higher process efficiency. Again, the polyelectrolyte charge and MW play an important role in the process, in view of their possible modification by the ozone.

Statistical analysis confirmed that DAF preceded by combined ozone conditioning and metal coagulant application, combined metal coagulant and cationic polyelectrolyte coagulant aid, and combined ozone conditioning, metal coagulant and cationic polyelectrolyte coagulant aid, in all cases outperformed DAF with metal coagulant application only. Ozone and polyelectrolyte had a statistically significant effect on treatment efficiency. Ozone and polyelectrolyte treatment had a significant effect on the particle removal efficiency irrespective of the initial particle count, while initial turbidity and polyelectrolyte treatment had a significant effect on the turbidity removal efficiency irrespective of the ozone treatment. No significant efficiency differences were detected between the above combined treatments.

**KMnO₄ conditioning** is attractive because of its oxidative capacity without the hazardous by-products formation, such as bromate formation in the case of ozonation. The KMnO₄ induced flocculation efficiency improvement is based on a range of process mechanisms which are often similar to the ones encountered with ozonation. KMnO₄ also causes algae stress and the release of EOM and IOM biopolymers, as verified by particle count, UV₄₅₀ nm absorbance and DOC measurements. The released EOM and IOM act as biopolymers and promote spontaneous micro-flocculation even before any coagulant addition, as verified by particle size analysis. Under normal pH conditions the colloidal (0.3-0.4 μm size) hydrous MnO₂ is formed. The negatively charged MnO₂ exhibits a high adsorption capacity for organic and inorganic particles and adds to the concentration of suspended particles, which reinforces the positive flocculation effect of any oxidant. Although the attachment of MnO₂ to algae tended to increase their negative surface charge presumably creating unfavourable coagulation conditions, the overall algae removal efficiency was similar to or higher than the one achieved with the iron coagulant only. The optimal permanganate dose (0.7 mg KMnO₄/L) for the model water conditions coincided with the visually determined permanganate demand (no pink colour observable after DAF). It resulted in 49% particle removal and 47% turbidity removal, compared to 40% and 44% achieved by the Fe(III)
coagulant alone. The KMnO₄ conditioning option proved significantly less efficient than the ozone conditioning, especially in terms of particle removal. The relatively high standard deviation of the efficiency results, as well as the occasional change of the permanganate demand, suggested that the organic matter concentration and composition, play an important role in defining the permanganate demand, its chemical effect and the resulting DAF efficiency. The optimal flocculation Gt range was related to the flocculation and removal of the colloidal MnO₂ and was 60,000 (typically G=70 s⁻¹, t=15 min).

The Mn and coagulant concentrations in the DAF effluent at the optimal permanganate dose were higher than their MAC values. This suggested that cationic polyelectrolytes could reduce the electrostatic repulsion between the oppositely charged Mn and Fe colloids. The DAF particle and turbidity removal efficiency in the case of cationic polyelectrolyte Superfloc C-573 coagulant aid application resulted in significantly better efficiency than was achieved in the case of iron coagulant only, or in the case of the combination of KMnO₄ conditioning and iron coagulant. A particle and turbidity removal efficiency of 95% and 86% respectively, were achieved with 0.5 mg Superfloc C-573 as coagulant aid, applied in combination with permanganate and Fe(III) coagulant. A 5-25% improvement of turbidity removal efficiency was also noted in comparison with the iron coagulant and cationic polyelectrolyte combination. The observed improvement was achieved via improved removal of both the Fe and Mn residuals. The option of lowering the residual Mn by the reducing agent Na₂SO₃ proved potentially viable. In any case, other studies proved that residual MnO₂ can be efficiently removed in a final filtration step.

Appendix 4.2 synthesizes the DAF particle and turbidity removal efficiency achieved under different treatment combinations.

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### Experimental conditions for different treatment combinations

<table>
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<th>CONDITIONS</th>
<th>O&lt;sub&gt;3&lt;/sub&gt; (mgO&lt;sub&gt;3&lt;/sub&gt;/mgTOC)</th>
<th>KMnO&lt;sub&gt;4&lt;/sub&gt; (mg/L)</th>
<th>Contact time (min)</th>
<th>Contact pH</th>
<th>Fe(II) (mg/L)</th>
<th>Poly. (mg/L)</th>
<th>Coag. G (g/L)</th>
<th>Coag. t (sec)</th>
<th>Coag. pH</th>
<th>Flocc. G (g/L)</th>
<th>Flocc. t (min)</th>
<th>R (%)</th>
<th>P (kPa)</th>
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<td>STOICHIOMETRY EXP.</td>
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<td>O&lt;sub&gt;3&lt;/sub&gt; COND. + POLY (C.A.)</td>
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<td>1.5; 3.0; 4.5</td>
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<td>1,000</td>
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<td>7.5 ± 0.2</td>
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<td>+ 500</td>
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<td>7.5 ± 0.2</td>
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<td>1,000</td>
<td>30</td>
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(C.A.) : Coagulant aid; (S.C.) : Sole coagulant; Poly. : Polyelectrolyte; Coag. : Coagulation; Flocc. : Flocculation

**Comment:**
- + 500 : Coagulation G value in case of polyelectrolyte as coagulant aid, applied after 30 s at G of 1,000 s<sup>-1</sup> for the FeCl<sub>3</sub>
- + 30 : Coagulation time in case of polyelectrolyte as coagulant aid, applied after 30 s at G= 1,000 s<sup>-1</sup> for the FeCl<sub>3</sub>
APPENDIX 4.2  Particle and turbidity removal efficiencies for different treatment combinations.

![Graph showing particle and turbidity removal efficiencies.]

Fig. 4.32  DAF particle and turbidity removal efficiency for different treatment combinations.

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>Fe(III) (mg/L)</th>
<th>Superfloc C-573 (mg/L)</th>
<th>Wisprofloc-P (mg/L)</th>
<th>O₂ (mg O₂/mg TOC)</th>
<th>KMnO₄ (mg/L)</th>
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Chapter 5

ALGAE LADEN WATER TREATMENT BY DISSOLVED AIR FLOTATION (DAF) - PILOT PLANT RESULTS

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ABSTRACT: Based on previous bench-scale dissolved air flotation (DAF) studies with model water (tap or reservoir water spiked with laboratory cultured *Microcystis aeruginosa*), DAF + (post) filtration pilot plant research was conducted using eutrophied reservoir water with a naturally occurring bloom of the same alga. The DAF removal of the algae was optimised, and the DAF + filtration process was compared with a full-scale sedimentation + filtration process scheme. Process variables included coagulant dose, coagulation pH, flocculation time and energy input, flocculation mode (one-, two- and three-stage flocculation), the application of organic and synthetic polyelectrolytes as coagulant aids, DAF recirculation ratio, etc. The application of ozone and KMnO₄ was tested in the context of algae conditioning and improved coagulation/flocculation and down-stream DAF + filtration effectiveness. The assessment of the process efficiency and kinetics was based on particle count and computer image analysis, in addition to commonly applied analytical techniques such as turbidity, residual coagulant, dissolved organic carbon (DOC), and electrophoretic mobility (EM). Similarly, the MFI (Modified Fouling Index) was measured. Results indicate the possibility of producing water of high quality after filtration, though the achievement of an appropriate MFI value (<5 s/L²) remains problematic. Suggestions are given for the appropriate approach to achieve it, including further optimisation of the agglomeration (coagulation/flocculation) process, application of conditioning oxidants like ozone or KMnO₄, and (post)filtration optimisation.

5.1 INTRODUCTION

Within the context of the research on the relevance and removal of cyanobacteria in water treatment (Chapters 1, 3 and 4), pilot plant investigations were conducted on location of the 'Princess Juliana' water treatment plant of the Rhine-Kennemerland Water Transport Company (WRK III) in Andijk, the Netherlands. The main goal of this investigation was to study the removal of naturally occurring cyanobacteria by dissolved air flotation (DAF). The eutrophic status of the IJssel Lake which replenishes the raw water reservoir, causes in late summer or early autumn cyanobacteria blooms of mostly *Microcystis aeruginosa*, a highly versatile and competitive species. Fig. 5.1 shows representative algae related parameters for the reservoir water quality for 1995. Two seasonal peaks of total chlorophyll are observed, one in early spring (ascribed to diatoms, mostly *Melosira* spp.) and one in late summer or early autumn (ascribed to the cyanobacterium *Microcystis* spp.). Much higher algae counts are registered during cyanobacteria blooms, these representing more than 99% of the overall algae count during these periods, and contributing to high chlorophyll values and algal volume. This situation results in numerous treatment problems, as well as a deteriorated product water quality. The problems include increase of required coagulant dose, shorter filter runs due to filter blockage, increased backwash water needs, algae as the source of trihalomethane formation (during short periods of NaOCl application to prevent mussels growth, a practice which has recently been abandoned), increased MFI (Modified Fouling Index) [1] and AOC (Assimilable Organic Carbon) [2] values of the product water [3], and algae passing through treatment in excessive quantities [4].

The integral water treatment process of the WRK III treatment plant relies on an efficient combination of reservoir water quality management, and water treatment. The 20 m deep reservoir with a retention period of 20 days (for an installed production of 12,000 m³/h) is periodically mixed with air to avoid stratification. FeSO₄ (average 5 g Fe(II)/m³) is dosed in the
reservoir mostly to promote phosphorus precipitation and algae growth reduction, as well as settling of algae within the reservoir itself. This technique is able to more than halve the original IJssel Lake algae concentration, which periodically reaches several hundred µg of chlorophyll/mL. The treatment process comprises microstrainers (one street with 35 µm, the two others with 200 µm mesh) (Fig. 5.2), coagulation/flocculation (coagulant Fe₂(SO₄)₃ with a dose 15-20 g Fe(III)/m³, maximum 43 g Fe(III)/m³; cationic polyelectrolyte Wisprofloc-P as coagulant aid with dose 0.1-0.2 g/m³, maximum 0.5 g/m³; and with pH correction by dosing Ca(OH)₂ (Fig. 5.3), up-flow lamella sedimentation (Fig. 5.4), and up-flow filtration (one street with a two-layer filter with barite and granite, and the two others with a single sand bed) (Fig. 5.5). The plant delivers water to the steel industry 'Hoogovens' and the Provincial Waterworks of North-Holland which further uses the water for ground infiltration. The infiltration line additionally comprises granular activated carbon filtration (GAC). The primary purpose of this concept is replenishment of the dunes fresh ground water aquifers.

The large coagulant doses are applied mainly to cope with the high organic load of the raw water (DOC level of the raw water during the experimental period ranged 5.0 - 14.4 g C/m³). They result in good product water, however, during the algae bloom periods they have to be substantially increased. This results in high production costs, which periodically even double.
**Fig. 5.2** The microstrainer units of the WRK III treatment plant at Andijk.

**Fig. 5.3** The flocculation units of the WRK III treatment plant at Andijk.
Fig. 5.4 The lamella sedimentation units of the WRK III treatment plant at Andijk.

Fig. 5.5 The up-flow rapid sand filtration units of the WRK III treatment plant at Andijk.
The most critical product water quality parameters related to the ground water recharge are the MFI and the AOC. The first defines the clogging capacity of the water, while the second defines its bacteriological after-growth potential. Recently, the required product water MFI value was set at 5 s/L². Together with the ambitious guideline of 10 mg AOC/m³, which roughly corresponds to the low value of 0.3 mg chlorophyll-a/m³[5], this poses increasingly difficult demands on the existing production, especially during cyanobacteria blooms (Fig. 5.6). The granular activated carbon (GAC) filtration is applied before infiltration in order to reduce pesticides with an additional beneficial side effect of AOC reduction.

![Graph showing Turbidity, residual Fe (total) and MFI (modified fouling index) for the WRK III filtrate.](image)

Fig. 5.6 Turbidity, residual Fe (total) and MFI (modified fouling index) for the WRK III filtrate.

This study investigates the applicability of the DAF process for algae removal on pilot plant scale on this reservoir water. It addresses DAF pilot plant optimisation (alone, and in combination with subsequent up-flow filtration), and comparison with the existing sedimentation + filtration full-scale treatment. For this purpose, the same coagulant used in the full-scale plant is considered (Fe₂(SO₄)₃ · 9H₂O). The same applies for the coagulant aid Wisprofloc-P, while based on positive results from earlier bench-scale experiments with model water (Chapters 3 and 4) Superfloc C-573 is also considered.

Commonly, conditioning of the water by microstraining (usually of mesh size ≥35 μm) is used as an initial barrier for coarse suspended matter in water treatment plants, thus lowering the load on subsequent treatment. This is also the case at the WRK III treatment plant. Microstrainers are particularly efficient in removing zoo-plankton and larger filamentous and chain-forming algal species; the retention of smaller algae varies as a function of their size and shape [6].

Although the potential benefits of oxidants such as chlorine, chlorine dioxide, ozone, hydrogen peroxide and potassium permanganate on the agglomeration phase have been recognised (Chapter 4) [7, 8, 9, 10, 11], their application has been restricted due to the formation of
hazardous by-products, notably trihalomethanes, haloacetic acids and haloacetonitrils by chlorine application, chlorite by chlorine dioxide application, and bromate by ozone application to waters rich in bromide [12]. This study aims at investigating ozone and KMnO₄ particle (algae) conditioning in the context of more efficient DAF on a pilot-plant scale, considering the potential disadvantages related to their application.

5.2 METHODS AND MATERIALS

The research was conducted on the premises of the 'Princess Juliana' (WRK III) treatment plant, situated on the shores of IJssel Lake in Andijk, the Netherlands. Raw water is subjected to settling within the raw water reservoir after dosing of FeSO₄. For experiments, water was abstracted from a location behind the microsieves. This is the same water which is further pumped to the full-scale sedimentation + filtration treatment. The research was conducted over a two year period. In the first year (September-November, 1995) it coincided with a cyanobacteria bloom of M. aeruginosa (Fig. 5.1), a common species for this period of the year. The second year (August-October, 1996) was characterised by a slightly lesser algae activity, but algae were still present in bloom [13] concentrations and chlorophyll-a levels reached 60 µg/L (average 29.3 µg/L).

5.2.1 Pilot plant experimental set-up

The experimental work was conducted with a commercial DAF pilot plant (PURAC, Sweden) (Fig. 5.7).

![Image](image_url)

**Fig. 5.7** View of the micro-strainer unit and the DAF pilot plant container with the filter column in the front, at the WRK III site.
The maximum capacity of the plant was 13 m$^3$/h, however, it was operated at $Q=4-6$ m$^3$/h in order to avoid air bubbles being carried over into the effluent. The DAF unit itself comprised a 1 m$^3$ stainless steel tank (Fig. 5.8) with four needle valves located at the bottom of the inlet for the recycled flow re-introduction.

5.8 The DAF pilot plant tank with the raw water inlet, chemicals dosing points and flash mixing (Kenics type, Purac, Sweden) on the left and the sludge pump at the bottom.

A variable level effluent outlet and automatic periodical sludge scraping were incorporated in the pilot plant (Fig. 5.9). Two options for coagulation were provided, a Kenics type in-line mixer and a flash mixing unit, while one-, two- or three-stage flocculation could be applied, each provided with variable speed mixers. A fully automated system provided the pumping, saturation and re-introduction of the recycled flow (Fig. 5.10). The product water was partly discharged, while the remaining part (0.4 m$^3$/h) was carried over to a transparent PVC up-flow filter column (Fig. 5.11).

The pilot filter was run in up-flow mode and had a multiple layer filling (simulating the full scale plant filters) with 30 cm gravel ($d=15-25$ mm), 30 cm barite ($d=5-10$ mm), 50 cm larger size granite ($d=1.2-2.0$ mm) and 75 cm fine granite ($d=0.5-0.95$ mm) layers. The filtration rate was kept constant at 10 m/h, simulating full-scale plant conditions. The filter was backwashed after
each run according to the full-scale filters backwash procedure, using air (from 0-70 m/h in the first 15 min), air (70 m/h) and water (the backwash rate rising from 0-20 m/h in the next 15 min) and water alone (in the next 30 min, the backwash rate rising from 20-108 m/h in the first 10 min of this period, the latter value being applied in the following 20 min period). After a series of experiments it was concluded that the DAF reached steady state very fast, approximately 45 minutes after start-up. In cases when DAF alone was evaluated, sampling for each experimental run was done after one hour from start-up. In cases when the DAF + filtration line was investigated, samples were taken after two hours from start-up. The effect of a longer filtration time was also investigated, and in this case samples were taken on an hourly basis for a maximum period of eight hours. During the pilot plant investigations period, the full-scale plant was not operating at its design capacity of 12,000 m³/h, but dropped from an initial 7,120 to 5,560 m³/h, with an accompanying filtration rate of approximately 10 m/h (September-November, 1995). Although no adequate base-line values existed, it may be assumed that the low production rate had a beneficial effect on the effluent quality during that period.

Fig. 5.9 The automatic sludge scraping unit of the DAF tank.

Fe₂(SO₄)₃ · 9H₂O was used as coagulant in a dosage range of 0-20 g Fe(III)/m³. pH in coagulation was set at pH 8 using Ca(OH)₂, as in the full-scale process. The organic cationic polyelectrolyte Wisprofloc-P and the synthetic cationic polyelectrolyte Superfloc C-573 were tested in the concentration range of 0.1-0.7 g/m³. The Kenics static mixer was used for the rapid mix with a calculated G value of ~3,500 s⁻¹ for a flow of 4.6 m³/h. Different flocculation time, energy input (G value) and flocculation sequence (one-, two- and three-stage flocculation) were
tested; the values were partly dictated by the technical provisions of the pilot plant. In the discussion section the applied flocculation time is denoted as $t_i$, while the flocculation energy input is denoted as $G_i$, the subscript ‘$i$’ signifying the flocculation stage.

Fig. 5.10 The automated DAF saturation unit of the pilot plant.

The recirculation ratio ($R$) in the DAF unit was set at 5, 7 and 10%, while the saturator pressure ($P$) was 500 kPa. The water temperature decreased from 16.7°C to 10.1°C in 1995, and from 16.4°C to 12.9°C in 1996, over the experimental period.

For ozone production, the Trailigaz LABO LO ozone generator was used (Fig. 5.12). A 4.5 m vertical, transparent PVC column of 135.5 mm diameter and allowing a contact time of 3.5 min (at $Q_{max} = 1.14 \text{ m}^3/\text{h}$) was used as a continuous-flow ozone reactor. Potassium permanganate (0.0021M working solution) was dosed immediately before pH correction and coagulant addition, allowing for very short contact times ($< 1 \text{ s}$) before coagulation and flocculation. This approach was preferred to avoid the extensive deposition of MnO$_2$ precipitates on the tank and walls.
Fig. 5.11 The multiple layer up-flow rapid filtration unit of the DAF + filtration pilot plant.

Fig. 5.12 The ozone production and metering units, part of the pilot plant set-up.
5.2.2 Analytical techniques

The process efficiency evaluation was based on turbidity (Sigrist L-65, Switzerland) and particle count of particles of size $>$ 2.75 $\mu$m (HIAC-Royco PC-320, USA). The notation T and PC used in the graph captions represents the initial turbidity and particle count, respectively. For particle count of particles in the size range of 0.3-5 $\mu$m the Particle Measuring Systems Inc./Liquid Batch Sampler LBS-100, and the Microlaser Particle Spectrometer (Boulder, Co., USA) were used. An inverted microscope (Zeiss Axiovert 135, Germany) was used for sample inspection. Residual coagulant (Fe$_{total}$) and manganese were measured by atomic absorption spectrometry at 248.3 nm for iron (NEN 6460) [14] and 279.5 for manganese (NEN 6466) [15]. Electrophoretic mobility was measured with a Tom Lindström AB-Repar apparatus. The transferred ozone concentration was determined by measuring the O$_3$ concentration in the inlet and outlet air/ozone gas mixture, by the iodometric method [16]. Bromate was measured by ion-chromatography [17]. The MFI measurements were performed using the KIWA N.V. Research and Consultancy standard MFI measurement apparatus (Fig. 5.13) [1]. Finally, computer image analyses were performed with the Mini-Magiscan, IAS 25/IV25 Joyce-Loebl Ltd., UK (Fig. 3.12, Chapter 3).

Fig. 5.13 The KIWA N.V. Research and Consultancy standard MFI measurement apparatus, with the filter column in the background.
Chapter 5 - Algae Laden Water Treatment by Dissolved Air Flotation (DAF) - Pilot Plant Results

The image analysis results are presented in the form of particle volume distributions. The volume distributions represent the volume of recorded particles in size ranges of 10 μm width for a specific sample. For this purpose, the recorded particles or floc material were approximated to spheres. The analyses were performed on fresh as well as on photographed samples [18, 19].

Here, preference was given to the latter, because this enabled multiple registration of relevant and representative situations along the treatment line without the risk of disturbing the process or the quality of the sample. For this purpose, a specially devised flat photo cell was connected at different locations of the pilot plant unit and samples were photographed before and after flocculation, and after treatment. In the case of DAF, the released air bubbles were also photographed and analysed. Professional high resolution black-and-white film AGFA 25 or Kodak TMAX 100 was used for the purpose, while forced development was applied for film processing. 30-100 fields, or more than 500 particles of each frame were processed and analysed, using a ccd-camera (604*288 pixels) mounted to a Nicon Optiphot microscope (at 40x magnification). The size limit of the set-up was 1.9 μm. The software package Genias25 developed by Joyce-Loebl Ltd., UK (Version 2.0, 1990) was used for data processing.

The presented experimental results emerge from duplicate or multiple experiments. Statistical analysis of data was performed with the Statistica software package. One and two way ANOVA followed by multiple comparison and regression analysis among treatment results were performed where appropriate.

5.3. RESULTS AND DISCUSSION

5.3.1. Coagulation conditions

a. Coagulant dose

Bench-scale experiments with model water (tap water spiked with laboratory cultured M. aeruginosa) showed that the DAF optimal dose was two to three times lower than the one for sedimentation, whilst the effluent quality in terms of the removal efficiency was comparable (Chapter 3) [20]. Pilot plant DAF without the use of coagulant resulted in poor turbidity (6.3%) and particle (19.5%) removal (Fig. 5.14), emphasizing the need to first destabilise - coagulate suspended material [19, 20, 21, 22, 23]. Increase of coagulant dose increased process efficiency. The highest coagulant dose tested was 20 g Fe(III)/m³ and efficiency continued to increase (up to 99.3%) without a clear 'optimum' being reached. A dose of 7 g Fe(III)/m³ consistently produced turbidity removal in the range of 84.9-93.2% (mean value of 89.3%) and particle removal efficiency of 87.7-97.5% (mean value of 94.5%). Multiple regression analysis (results from seven experiments) for particle removal efficiency ($r^2=0.48$, as a dependent variable) and initial particle count and coagulant dose (as independent variables) yielded results suggesting that the particle removal efficiency was significantly affected by both the initial particle count ($P=0.0015$) and the coagulant dose ($P=0.00072$). The same analysis for turbidity removal efficiency ($r^2=0.53$) showed that it was significantly affected by the coagulant dose ($P=0.000001$) and insignificantly affected by the initial turbidity ($P=0.37$).
Fig. 5.14 DAF removal efficiency as a function of coagulant dose (duplicate experiment). Conditions: pH 8, two-stage flocculation with $t_1 = 18.2$ min, $G_1 = 50$ s$^{-1}$ and $t_2 = 3.8$ min, $G_2 = 30$ s$^{-1}$, $R = 7\%$, $P = 500$ kPa, $T = 7.8$ FTU, $PC = 12,580$/mL.

The average DAF efficiency for the coagulant dose of 7 g Fe(III)/m$^3$ tended to be slightly lower compared to the mean full-scale sedimentation efficiency registered in the same period: turbidity removal of 96.0% and particle removal efficiency of 97.3%. The sedimentation unit, however, was operated with a combined coagulant dose of 20-24 g Fe(III)/m$^3$ and 0.2-0.5 g W-P/m$^3$ cationic coagulant aid. The comparatively lower DAF efficiency can partly be attributed to the higher residual (colloidal) iron. The residual (total) iron after DAF decreased with increase of the coagulant dose, reaching 1.05 g Fe/m$^3$ for the 20 g Fe(III)/m$^3$ dose, as compared to the average 0.39 g Fe/m$^3$ after sedimentation. The DOC removal at the 7 g Fe (III)/m$^3$ dose was also found lower than observed in the full scale plant at 20-25 g Fe(III)/m$^3$ (7-20% and 25-35%, respectively). It is suggested that the precipitating iron species formed during the sweep coagulation process partially form complexes with the abundantly present organic matter. The high coagulant doses applied before the sedimentation are responsible for the more comprehensive sweep coagulation and consecutive higher degree of turbidity and iron removal compared to the three times lower DAF coagulant dose. The colloidal character and size of the organo-iron complexes coincides with the size range ($< 1$ μm) for which Brownian diffusion plays a major role in the particle-bubble attachment, which renders them more difficult to remove by DAF than particles in the size range larger than 1 μm [22]. At a coagulant dose which lies between 10 and 15 g Fe(III)/m$^3$ the DAF particle removal efficiency (of particles $> 2.75$ μm) surpassed the one obtained by the full-scale sedimentation (for identical raw water quality conditions), indicating more efficient particle coagulation. However, this improvement of performance did not apply for the turbidity and residual iron.

The turbidity removal efficiency of the final filter for a coagulant range of up to 20 g Fe(III)/m$^3$ was 95.5-98.4%, while the particle removal efficiency was 96.8-99.7%, increasing with
increasing coagulant dose. It is suggested that the residual Fe coagulant after DAF was mainly in the organo-iron complex form of a colloidal size, which is equally difficult to remove by filtration; thus, the increase of the filtration efficiency could be ascribed mainly to the better water quality obtained after DAF at the higher coagulant doses. The filter effluent turbidity corresponding to these removal efficiencies was 0.1-0.35 FTU; according to the guidelines of the Association of Dutch Water Supply Companies (VEWIN Aanbevelingen, 1993) this is acceptable from the point of view of product water quality (<0.8 FTU if no disinfection is applied and <0.2 FTU in case of disinfection), and is comparable with the full-scale plant filtrate turbidity.

b. Coagulation pH

Due to the high buffering capacity of the raw water and limitations on the available dosing equipment, the lowest tested pH was 6.35. Fig. 5.15 represents the turbidity and particle removal efficiency under different pH conditions. The highest turbidity and particle removal efficiency was obtained at pH 6.35 (93.2% and 97.5%, respectively). The same applied for DOC removal (33%). This is in accordance with the experiments on model water (Chapter 3), as well as with theory, which suggests that adsorption coagulation preferentially occurs in this pH range at a medium to low coagulant dose and supports the otherwise dominant sweep coagulation. Electrophoretic mobility (EM) measurements, however, did not confirm complete charge neutralisation, contrary to results with model water (Chapters 3 and 4) [19, 23]. The lowest DAF turbidity, residual iron and DOC removal were obtained at pH 8. As for particle removal, the lowest efficiency was obtained at pH 9, possibly due to the precipitation of calcite particles under alkaline conditions. These particles have a size similar to that of Microcystis (≈ 10 μm, [12]). Final filtrate quality was again influenced most strongly by the DAF effluent quality.

![Diagram](image_url)

**Fig. 5.15** Variation of coagulation pH in DAF + filtration. Conditions: 7 g Fe(III)/m³, two-stage flocculation with t₁=18.2 min, G₁=50 s⁻¹ in the first, and t₂=3.8 min, G₂=30 s⁻¹ in the second stage, R=7%, P=500 kPa, T=5.8-6.9 FTU, PC=12,100-18,100/mL.
5.3.2 Flocculation conditions

a. Flocculation time

Research and practice have yielded contradictory conclusions with respect to optimal flocculation time and energy input in case of DAF. Janssens [21] and Malley and Edzwald [24] stated that flocculation times as short as 5 minutes can suffice for efficient down-stream DAF. Our bench-scale experiments on model water on the other hand, have shown that flocculation times longer than 10 minutes did increase DAF process efficiency (Chapter 3), but only by ≈5% [20]. On the other hand, full-scale DAF plants are rarely operated with flocculation times shorter than 20-30 minutes [4, 25].

![Graph showing particle and turbidity removal vs. flocculation time](image)

Fig. 5.16 Variation of flocculation time for DAF + filtration. Conditions: 7 g Fe(III)/m³, G=50 s⁻¹, R=7%, P=500 kPa, T=5.8-6.9 FTU, PC=12,100-18,100/mL.

Results of pilot plant optimisation of flocculation time are presented in Fig. 5.16. No clear optimum was established, the DAF efficiency rising with longer flocculation times. Flocculation times shorter than 15 minutes produced a DAF effluent of inferior quality regarding turbidity, particle count and residual coagulant. The filtrate quality after run time of two hours was similar for different flocculation times, although longer flocculation times will most probably enable longer filter runs (before filter breakthrough or blockage occurs). For further experiments a flocculation time in the range of approximately 20 minutes was chosen, which was partly determined by limitations of the pilot plant.

b. Flocculation energy input

Literature commonly states that relatively high G values (e.g. G=50-100 s⁻¹) produce small, strong and dense flocs, able to resist the shear applied when the DAF recycle stream is re-introduced in the flotation chamber via the nozzles or needle valves, thus favouring DAF
efficiency [22]. Our experiments on model water showed that this may need further confirmation (Chapter 3), as the overall DAF efficiency is influenced by a combination of factors, of which the relation between floc size distribution, and floc density and strength are of primary importance.

Two sets of pilot plant experiments were conducted, one with a short flocculation time of 5 min and a different flocculation G value (G = 10, 30 and 50 s\(^{-1}\)), and a second with a flocculation time of 20 min and different flocculation G value (G = 10, 30, 50 and 70 s\(^{-1}\)). Turbidity and particle removal efficiency for these experiments are presented in Figs. 5.17 and 5.18.

![Graph](image)

**Fig. 5.17** Variation of flocculation G value for flocculation time of 5 min. Conditions: 7 g Fe(III)/m\(^3\), pH 8.4, R = 7%, P = 500 kPa, T = 6-7 FTU, PC=14,800-18,100/mL.

![Graph](image)

**Fig. 5.18** Variation of flocculation G value for flocculation time of 20 min. Conditions: 7 g Fe(III)/m\(^3\), pH 8.4, R = 7%, P = 500 kPa, T = 7.7 FTU, PC=13,460/mL.

The process efficiency for the short flocculation time of 5 min rose with increasing G value (from
78.1-85.5% for particle removal and from 63.6-66.0% for turbidity removal. It is suggested that the contact opportunities during the short flocculation time were insufficient to flocculate the colloidal and particulate matter by the precipitating coagulant. This was supported by the high residual iron of more than 2.5 g Fe(III)/m³. Increase of the G value resulted in higher DAF efficiency, including a lower residual iron value. The DOC removal was low, typically below 10% (6-7%).

In the case of the longer flocculation time of 20 minutes the turbidity removal efficiency rose slightly with increase of the G value, reaching its 'optimum' (89.9%) at G=50 s⁻¹, while the particle removal efficiency slightly decreased with increase of the G value (from 96.6 to 94.5%). This was accompanied by increased residual Fe, and decreased DOC removal (from 20 to 12%).

Image analysis data of raw and flocculated water with flocculation G=10, 30 and 50 s⁻¹ (Fig. 5.19) show that the inverse relation between floc size and flocculation energy input is less pronounced than in the case of flocculation of the model water (Figs 3.6 and 3.7). This difference is suggested to be related to the different model water and reservoir water quality, especially the TOC and DOC concentration and composition, and the organic matter - metal coagulant interactions. It is to be considered that the particles after coagulation of the reservoir water are of colloidal and suspended size, including organo-iron complexes <1 μm, and algae >1 μm, however, of different quality (charge and steric phenomena) and size (fairly monodispersed in case of the model water and heterodisperse in case of the reservoir water) characteristics, and of significantly higher concentrations than in the model water circumstances.

![Diagram](image)

Fig. 5.19 Particle volume distribution as a function of flocculation G value. Conditions: 10 g Fe(III)/m³, flocculation time t=22 min. pH 7.8-8, R=7%, P=500 kPa, T=6.8-7.9 FTU, PC=18,040-20,680/mL.

According to the heterodisperse curvilinear approach to (turbulent) flocculation modelling [26], the trajectory of one particle approaching another is curvilinear and the velocity gradient G is not
of primary significance compared to the rectilinear model of Smoluchowski. Accordingly, Brownian motion and differential settling control the collision opportunities of most combinations of particle sizes. Low water temperature and hence high viscosity lower the collision rate. The energy input \( G \) is of relevance only if both particles are larger than 1 \( \mu \text{m} \) and have a size ratio of approximately 10. Here (Fig. 5.19), the collision rate between particles in the size range of up to 50 \( \mu \text{m} \) seemed to be affected indeed by the energy input, the increase of \( G \) resulting in more successful agglomeration.

The reduction of the number frequency of particles of size <50 \( \mu \text{m} \) with increase of the \( G \) value (not presented here), was more pronounced than the reduction in volume, due to the significantly smaller contribution of the small particles (<50 \( \mu \text{m} \)) to the total particle volume as compared to the larger particles and flocs. On the other hand, the residual iron rose and DOC removal decreased with increase of the \( G \), suggesting that the successful collision rate of the smaller colloidal particles, to which the organo-iron complexes belong, was negatively affected by the higher \( G \). The limitation of the image analysis system to particles larger than 1.9 \( \mu \text{m} \) impedes further discussion. The flocculation between particles of very different sizes (as in our case) is predicted to be much slower by the curvilinear flocculation model, which could explain the increase of process efficiency with increase of flocculation time (Figs. 5.16, and 5.17 and 5.18).

The documented presence of NOM in the form of fine matrices or meshes of filaments in waters of similar quality [27, 28] may have also played a role in the flocculation process of the reservoir water and additionally influenced the floc volume distribution. The role of these structures, however, is difficult to interpret in the context of the different \( G \) values.

The particle (floc) distributions obtained for different flocculation \( G \) values did not significantly differ from each other (for particles of size > 1.9 \( \mu \text{m} \)), and the same holds for the DAF efficiency. It is suggested that the slight increase of DAF particle removal efficiency at lower \( G \) was partly due to the lighter floc structure obtained at the low flocculation \( G \) values.

c. Flocculation mode

The optimal flocculation mode similarly has raised contradictory experiences between practice and theory [4, 20]. Tapered flocculation is often applied in combination with DAF although there is little theoretical support for this choice. Tapered flocculation generally results in a floc size distribution and characteristics favourable for sedimentation. For the research here, three flocculation modes were tested: single-stage flocculation \((t_1 = 3.8 \text{ min}, G_1 = 30 \text{ s}^{-1})\), two-stage flocculation \((t_1 = 18.2 \text{ min}, G_1 = 50 \text{ s}^{-1}, t_2 = 3.8 \text{ min}, G_2 = 30 \text{ s}^{-1})\) and three-stage flocculation \((t_1 = 10.8 \text{ min}, G_1 = 70 \text{ s}^{-1}, t_2 = 18.2 \text{ min}, G_2 = 50 \text{ s}^{-1}, t_3 = 3.8 \text{ min}, G_3 = 30 \text{ s}^{-1})\), determined by the pilot plant flow.

The first mode resulted in noticeably lower process efficiency (84.1% particle removal), especially in terms of residual turbidity (63.4% removal) (Fig. 5.20), accompanied by a high residual iron level of 3.35 g Fe (III)/m³. Again, it is suggested that the short flocculation time provided for insufficient contact opportunities between particles and for inefficient flocculation. The benefits of the additional third stage of flocculation were minor in terms of turbidity and particle count reduction, though it led to a residual iron level that was significantly lower (0.76 compared to 1.13 g Fe (III)/m³ for the two-stage mode). The DOC removal efficiency increased with the number of flocculation stages (and thus longer flocculation time) from 11.9-29.3%, the
Fig. 5.20  Particle and turbidity removal efficiency as a function of tapered flocculation mode. Conditions: 7 g Fe(III)/m$^3$, pH 7.8-8.0, R=7%, P=500 kPa, T=6.8-7.9 FTU, PC=18,040-20,680/mL.

Fig. 5.21  Particle volume distribution as a function of coagulant choice and flocculation stage. Conditions: 15 g Fe(III) vs. 15 g Fe(III) + 0.5 g C-573/m$^3$, pH 8, tapered flocculation with $t_1=18.2$ min and $G_1=50$ s$^{-1}$ in the first stage (S1) and $t_2=3.8$ min and $G_2=30$ s$^{-1}$ in the second stage (S2).
The particle volume distribution after each of the first two stages featured a noticeable increase of particle volume in the larger particle size range on account of a decreasing volume of the smaller particles, and the decreasing G value in the second flocculation stage (Fig. 5.21). However, there was little impact on the final DAF effluent quality after tapered flocculation as compared to that after single-stage flocculation with similar G value and flocculation time.

5.3.3 Application of polyelectrolytes as coagulant aids

The application of cationic polyelectrolytes as coagulant aid resulted in increased DAF (and sedimentation) efficiency in earlier bench scale experiments (Chapters 3 and 4) [19, 20]. Other positive experiences [29], as well as the actual operation practice at WRK III which applies the cationic polyelectrolyte Wisprofloc-P in its treatment (0.2-0.5 g/m³), suggested an opportunity for further research. Based on the bench-scale experiments with model water (Chapters 3 and 4) two cationic polyelectrolytes were chosen for evaluation: the organic Wisprofloc-P and the synthetic Superfloc C-573. The dosage range for both was 0.1-0.7 g/m³, in combination with 7 g Fe(III)/m³ (Figs. 5.22 and 5.23).

![Graph showing particle and turbidity removal vs. coagulant aid dose](image)

**Fig. 5.22** Variation of coagulant aid (Wisprofloc-P) dose. Conditions: 7 g Fe(III)/m³, two stage flocculation with t₁ = 18.2 min and G₁ = 50 s⁻¹ in the first, and t₂ = 3.8 min and G₂ = 30 s⁻¹ in the second stage, pH 8, R = 7%, P = 500 kPa, T = 4.6-7.5 FTU, PC = 13,730-19,370/mL.

The turbidity removal efficiency slightly decreased with increasing Wisprofloc-P dose (from 89.8 to 88.7%), while the opposite was noted for the particle removal efficiency (from 94.0 to 94.7%) and residual coagulant, suggesting that the polyelectrolyte residual is the probable cause for the turbidity increase.

In the case of Superfloc C-573, slightly better results were obtained (94.6-96.4% particle removal and 90.1-91.4% turbidity removal, see Fig. 5.23); the same was true when the results were compared to the case without coagulant aid (92.4% particle removal and 89.3% turbidity removal). The efficiency did not change noticeably with the coagulant aid dose. This contradicts the bench scale model water experiments (Chapter 3) in which quality improvement after
coagulant aid application was very significant (increase of approximately 40% for particle and 30% for turbidity removal efficiency). EM measurements showed that although the particles electric charge decreased (from -0.84 to -0.78 μm/s/V/cm for 7 g Fe(III)/m³ in combination with 0.5 g Superfloc C-573/m³, at pH 8), no complete charge neutralisation occurred as in the model water experiments. It is suggested that the abundant DOC present in the WRK III reservoir water exerted an additional demand for polyelectrolyte [30], reducing its availability for coagulation. This, and the relatively low coagulant dose of 7 g Fe(III)/m³ are probable causes of the comparatively low removal efficiency improvement.

Fig. 5.23  Variation of coagulant aid (Superfloc C-573) dose. Conditions : 7 g Fe(III)/m³, two stage flocculation with t₁=18.2 min and G₁ =50 s⁻¹ in the first, and t₂=3.8 min and G₂ =30 s⁻¹ in the second stage, pH 8, R=7%, P=500 kPa, T=6.5-6.7 FTU, PC =14,960-16,080/mL.

One way ANOVA for different treatment options (Fe and Superfloc C-573, with conditions as mentioned in Fig. 5.23) showed that DAF efficiency in the case of Superfloc C-573 showed no significant differences between the treatment options (P=0.98 for particle removal efficiency and P=0.97 for turbidity removal efficiency). Multiple regression analysis for particle removal efficiency (r²=0.1) showed that neither the initial particle count (P=0.89) nor the polyelectrolyte (P=0.11) was a significant factor in determining DAF efficiency. The same applies for the turbidity.

Fig. 5.21 represents particle volume distribution of flocculated water with and without the addition of coagulant aid. Improved agglomeration was achieved in the former case (0.5 g of Superfloc C-573/m³ and 15 g Fe(III)/m³) resulting in a more pronounced larger particle size fraction and a reduction of the smaller particles fraction. The increased concentration of particles in the 30-150 μm size range in the case of only 15 g Fe(III)/m³, changed when coagulant aid was added, resulting in denser floc structures with a slight increase of particles (flocs) in the > 150 μm range. In the DAF pilot plant study, the beneficial effect of the cationic polyelectrolyte application tended to be most evident for doses ≥0.5 g Superfloc C-573/m³ in combination with coagulant dose ≥15 g Fe(III)/m³.

However, two way ANOVA for the cases of a low coagulant dose of 7 g Fe(III)/m³, and combined coagulant dose of 7 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid, versus
a high coagulant dose of 15 g Fe(III)/m³, and combined coagulant dose of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid, showed that only the coagulant dose had a statistically significant effect ($P=0.034$) on the DAF efficiency (Fig. 5.24).

![Diagram](image)

**Fig. 5.24** Particle removal efficiency for different dosage combinations of coagulant and coagulant aid (including P-levels from the two-way ANOVA, number of experiments n=14).

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>Fe(III) (g/m³)</th>
<th>C-573 (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (DAF)</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>1' (DAF)</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>2 (DAF)</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>2' (DAF)</td>
<td>15</td>
<td>0.5</td>
</tr>
</tbody>
</table>

A high coagulant dose of 15 g Fe(III)/m³, and combined coagulant dose of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid, showed that only the coagulant dose had a statistically significant effect ($P=0.034$) on the DAF efficiency (Fig. 5.24).

![Diagram](image)

**Fig. 5.25** Particle removal efficiency for different dosage combinations of coagulant and coagulant aid, for the pilot plant DAF (DAF) and full-scale sedimentation (SED) (including the P-level from the one-way ANOVA, n=15).

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>Fe(III) (g/m³)</th>
<th>C-573 (g/m³)</th>
<th>W-P (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (DAF)</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 (DAF)</td>
<td>15</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>3 (SED)</td>
<td>20</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Finally, one way ANOVA for the particle removal efficiency achieved at the cases of the low coagulant dose of 7 g Fe(III)/m³, combined coagulant dose of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid, and the full-scale sedimentation (20 g Fe(III)/m³ and 0.2 g W-P/m³) showed that there was no statistically significant difference \( (P=0.073) \) between the three treatment options (Fig. 5.25). The results of both ANOVAs may have been influenced by the limited availability of replicates for the combined 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ option.

### 5.3.4 Particles (algae) conditioning

#### a. Ozone conditioning

The significance of the results from the pilot plant study on ozone conditioning was constrained by the technical limitations of the ozone pilot column. The maximum flow in the ozone column was 1.1 m³/h which led to long DAF retention times of approximately 1 hour and a deteriorated effluent quality due to particles settling within the DAF unit. On the other hand, the experiment allowed to quantify the bromate formation under the circumstances of the WRK III reservoir water (Fig. 5.26).

![Graph showing bromate (BrO₂⁻) concentration in DAF product water for different O₃ doses and pH](image)

**Fig. 5.26** Bromate (BrO₂⁻) concentration in DAF product water for different O₃ doses and pH (raw water TOC=6.2 g/m³).

The relatively high TOC concentration of the raw water (mostly DOC) imposed a need for adequately high ozone doses of typically 1.2-5.5 gr O₃/m³ [31]. The resulting bromate concentrations of 10-38 µg/L were all (except one) below the WHO provisional guideline value of 25 µg BrO₂⁻/L, however, higher than the European Union drinking water guideline of 10 µg/L, and far higher than the envisaged bromate standard for the Netherlands of 0.5 µg/L, or 5 µg/L where ozone is applied for disinfection.

The bromate formation via O₃ and OH⁻ mediated reactions is significantly affected by pH (Fig. [image link])
5.26); its concentration increases sharply with pH and ozone dose. Earlier bench-scale experiments confirmed that ozone as conditioner for algae removal by DAF yielded higher removal efficiency compared to treatment with coagulant alone (Chapter 4). Ozone dosages as low as 0.2 mg O₃/mg TOC (0.6 mg O₃/L) in combination with pH 7.5 resulted in significant DAF particle (algae) removal efficiency improvements of 40-50% (Chapter 4, Figs. 4.11 and 4.12). Use of cationic polyelectrolytes as coagulant aid further increased DAF efficiency typically by 5%. Scanning electron microscopy (SEM) of ozonated model water (Fig. 4.15, Chapter 4) showed that ozone affected the outer algal cell wall and damaged part of the algal cells. Leakage of the IOM that then acts together with EOM as natural coagulant aid has been proposed to be one of the main coagulation mechanisms [32, 33, 34, 35].

In the case of WRK III water, the 0.2 g O₃/g TOC corresponded roughly to a dose of 1.2 g O₃/m³, which at pH 7 resulted in pilot plant bromate levels approaching the EU guideline value of 10 μg/L. This promotes ozone conditioning at lower pH (<pH 7) as an attractive option in WRK III circumstances, especially in view of the possible accompanying reduction of the clogging capacity of the water [9], and improvement of organic matter (including pesticides) removal by the GAC filtration [36].

b. KMnO₄ conditioning

The pilot plant research confirmed the beneficial influence of this oxidant. KMnO₄ application proved to be beneficial under the conditions of the model water, however, its influence on the process efficiency was lower and less predictable compared to ozonation (Chapter 4) [35].

The DAF removal efficiency of particles larger than 2.75 μm (the lower size limit of M. aeruginosa) at a dosage of 10 g Fe(III)/m³ was comparable to or higher than the full-scale sedimentation performance with 24 g Fe(III)/m³ and 0.5 g Wisprofloc-P/m³ (i.e. 96.3% and 95.9% mean particle removal efficiencies). Additional KMnO₄ conditioning at 1.0 g KMnO₄/m³ tended to increase the DAF particle removal efficiency (97.7% mean particle removal), the results after DAF being consistently better than those of the full-scale sedimentation and at some occasions also better than the results after the full-scale filtration (maximum DAF particle removal efficiency of 99.7%). This enhanced performance should result in lower filter loading by particles larger than 2.75 μm. However, negatively charged MnO₂ colloids are formed that cause manganese concentration in the DAF effluent to over the 50 μg/l MAC, and thus, together with organo-iron complexes contribute to a higher residual turbidity after DAF. In order to further increase the DAF removal efficiency and improve the effluent quality, KMnO₄ was applied in combination with cationic polyelectrolytes Superfloc C-573 and Wisprofloc-P. Positive effects were achieved at polyelectrolyte dosage ≥0.5 g/m³ and coagulant dose ≥10 g Fe(III)/m³ . Figs. 5.27 and 5.28 represent an overview of the particle and turbidity removal efficiency results from this part of the research (1-4), compared to the full scale sedimentation (5) and filtration (6) processes.

The one-way ANOVA for different treatment options, including the full-scale WRK III sedimentation and filtration treatment (5 (SED) and 6 (FILTR) in Figs. 5.27 and 5.28), showed that treatment significantly affected both particle (P=0.00022) and turbidity (P=0.000001) removal efficiency. However, one-way ANOVA performed on only the DAF options (1 through 4 (DAF) in Figs. 5.27 and 5.28) yielded no statistically significant difference between the considered treatment options, either for particle (P=0.085) or for turbidity (P=0.686) removal efficiency.
Fig. 5.27 One-way ANOVA of the pilot plant (1-4 (DAF)) vs. full scale plant sedimentation (5 (SED)) and filtration (6 (FILTR)) particle removal efficiency (of particles >2.75 \( \mu \)m).

**ONE-WAY ANOVA : TURBIDITY P=0.00001**

Fig. 5.28 One way ANOVA of the pilot plant (1-4 (DAF)) vs. full scale plant sedimentation (5 (SED)) and filtration (6 (FILTR)) turbidity removal efficiency.
This suggests that the tendency that DAF improves particle removal efficiency after KMnO₄ conditioning, as well as the improvement after combined KMnO₄ conditioning and addition of cationic coagulant aid, were not statistically confirmed in the pilot plant operation. However, multiple comparison analysis (excluding the WRK III full-scale filtration) on particle removal efficiency yielded statistically significant differences only for treatment options 4 and 5 (the number of comparisons being 4, the comparisonwise error rate was $P=0.05/4=0.0125$, and since for treatment options 4 and 5 $P=0.0093$, thus $<0.0125$), approaching the comparisonwise error rate of 0.0125 in the cases of treatment options 1 and 4.

This suggests that the combined KMnO₄ and 0.5 g Superfloc C-573/m³ polyelectrolyte treatment performed statistically significantly better in terms of particle removal efficiency than the full-scale sedimentation, and that the combined KMnO₄ conditioning and >0.5 g Superfloc C-573/m³ polyelectrolyte treatment may be considered appropriate to significantly raise the DAF particle removal efficiency. The multiple comparison analysis on turbidity removal efficiency suggests that the full-scale sedimentation performed statistically significantly better than all the DAF options ($P<0.0125$), albeit at much higher coagulant dose. This is mainly due to the coagulation chemistry at the lower coagulant doses that are generally applied in the DAF process.

The KMnO₄ effect on coagulation and flocculation is considered a combined consequence of microorganism inactivation; modification of the algal cell wall and in-situ production of natural, algae derived coagulant aid; oxidation and subsequent adsorption of coagulation interfering organic matter; and accelerated flocculation because of increased particle concentration due to MnO₂ colloids (Chapter 4) [29, 37]. The main overall difference between DAF jar test experiments on model water and the pilot plant work, is that the latter provided consistently good effluent water quality, especially in terms of particles (algae) removal (94.9-99.7%), unlike the former which was characterised by variations in effluent quality and relatively low efficiency (27.0-88.2%). One of the possible causes of this phenomenon is the different NOM concentration and characteristics in the water used in the two experimental modes.

In case of the model water experiments (Chapter 3 and 4) the TOC concentration before spiking the water with the algae was in the range of 1.8-2.5 mg C/L, mostly comprised of DOC (>95%). This organic matter remained from the originally present organic matter in the (Biesbosch reservoirs) water after full treatment in the Kralingen water treatment plant (Rotterdam, the Netherlands). The treatment includes Fe (III) coagulation/flocculation, sedimentation, ozone application (3 mg O₃/L), rapid sand and granular activated carbon filtration. Since ozone generally reduces the molecular weight of NOM compounds and increases their functional group content, it is surmised that it also reduces the precipitating tendency of the remaining NOM molecules by the applied Fe (III) coagulant in the bench-scale experiments. Furthermore, the remaining NOM molecules after the full treatment likely lack functional groups that would enable sorption processes with the metal (coagulant) oxide surfaces [38]. After spiking the algae in this water, the TOC and DOC concentration rose to 2.3-3.0 mg C/L and 2.0-2.7 mg C/L, respectively. Thus, the algae and their EOM (as well as IOM in case of oxidants application) were probably the most significant portion of the organic matter exerting a coagulant demand and prone to react with the KMnO₄ in the bench-scale experiments. In these circumstances, KMnO₄ addition resulted in the creation of stress conditions for the algae and increased EOM and IOM concentrations, which coupled to other KMnO₄ induced mechanisms (Section 4.3.4.a) resulted in improved coagulation/flocculation and increased DAF efficiency. Since the impact of the conditioning process relied mostly on the quality of the cultured algae and their exudates (EOM and IOM
composition, dependant on algae age), occasional changes of permanganate demand were recorded, as well as a relatively large standard deviation of the DAF efficiency.

On the other hand, the reservoir water used in the pilot plant experiments was characterised by a TOC concentration in the range of 5-15 g C/m³, mostly comprised of DOC (90-95%). The relatively high DOC was comprised mostly of humic matter, which itself exerted a high coagulant demand. The importance of the OM content and composition in the presence of KMnO₄ conditioning, for the enhancement of coagulation, has been documented by others as well [39]. It is related to the documented existence of NOM in the form of fine matrices or meshes of filaments in waters of similar quality [27, 28]. These fine matrices can embed both algal EOM and IOM, and MnO₂ precipitates, and thus promote flocculation via a bridging mechanism. Thus, they are suggested as a factor which enhanced DAF pilot plant efficiency. It can also be surmised that the NOM fine matrices embedding the flocculated material form a gel-like structure which improves the particle-bubble attachment and DAF efficiency.

The particle count for size 0.3-5 µm showed that the effluent from the KMnO₄ + DAF + filtration scheme had a considerably higher particle count than that of the full-scale sedimentation + filtration scheme, especially in the colloidal size range <1 µm. It is suggested that the lower coagulant doses applied in the DAF (as compared to sedimentation), although efficient in destabilising particulate matter (including algae), could not provide complete sweep coagulation, especially with regard to the high DOC fraction of the NOM. Thus, it is the DOC rather than the particles that control the coagulant dose [40]. Here, the high particle count in the <1 µm size range is compounded by the residual colloidal MnO₂ (of typical size 0.3-0.4 µm) and the difficult to remove organo-iron complexes (of typical size <1 µm). On the other hand, the considerably higher coagulant doses in the full-scale sedimentation (24 g Fe(III) + 0.5 g Wispofloc-P/m³, against 10 g Fe(III)/m³ alone, or in combination with 1.0 g KMnO₄/m³ used in DAF) resulted in complete sweep coagulation and proved favorable for efficient sedimentation due to the very high particle concentration. This observation is supported by residual coagulant measurements that were considerably lower in case of the sedimentation.

This means that as measured against particle removal efficiency including particles in the 0.3-1 µm colloidal size range and the 1-150 µm algae representative size range, the best results were obtained by the sedimentation option (87.4%), followed by the pilot plant KMnO₄ + DAF (65.8%), and the pilot plant DAF without KMnO₄ conditioning (62.5%). Similar order of particle removal efficiency (0.3-150 µm) was noted for the different overall treatment options, although with smaller differences between each treatment option (92.7% for the sedimentation + filtration option, 88.8% for the pilot plant KMnO₄ + DAF + filtration option, and 86.1% for the DAF + filtration option). The particle removal efficiency for particles in the algal size range (>1 µm) of the DAF + filtration option achieved at higher coagulant (>10 g Fe(III)/m³) and coagulant aid (>0.5 g Superfloc C-573/m³) doses, alone or in combination with 1.0 g KMnO₄/m³ conditioning, was similar to that of the full-scale sedimentation + filtration option (24 g Fe(III) + 0.5 g Wispofloc-P/m³); however, this did not apply for the submicron particle size range. This suggests that due to the incomplete sweep coagulation achieved by the generally lower coagulant doses applied in the DAF, and the lower efficiency of the DAF unit in the removal of the colloidal particles in general [22, 41] (as compared to the favorable conditions created by the high coagulant doses in the sedimentation), the pilot filter in the DAF + filtration option was subjected to higher loads of colloidal matter, which will probably result in shorter filter runs [42, 43].
5.3.5 DAF recirculation ratio

Conservatively high recirculation ratio and saturator pressure proved to be of little influence on DAF efficiency in bench-scale model water experiments [41]. Similar results were obtained with the pilot plant (Fig. 5.29). Slightly better turbidity and particle removal efficiency was obtained at a recirculation ratio of 7% (86.3% and 95.6%, respectively), as compared to 5% (84.0% and 93.9%, respectively) and 10% (84.6% and 95.6%, respectively) for a constant pressure of 500 kPa. The recirculation ratio R and saturator pressure determine the ratio between bubble and particle concentrations and their size, and have often been suggested to determine the DAF efficiency. However, measurements and calculations on the DAF single collector collision efficiency model [41] suggest that only relatively low bubble concentration is obtained with R=5% and saturator pressure of 500 kPa and saturator efficiency of 90% (N_b=25,600 bubbles/ml of 62 μm mean size) compared to the high particle concentration N_p=16,650 particles/ml after flocculation at 10 g Fe(III) + 0.3 g Superfloc C-573/m³ (Fig. 5.23) which does not fully explain the overall high process efficiency. Most likely, it is again the NOM that accounts for the more efficient particle-bubble attachment in DAF.

![Graph](image)

Fig. 5.29  Particle removal efficiency after DAF and after filtration, as a function of recirculation ratio R. Conditions : 7 g Fe(III)/m³, pH 8, two-stage flocculation with t_1=18.2 min and G_1=50 s⁻¹ in the first stage, and t_2=3.8 min and G_2=30 s⁻¹ in the second stage, P=500 kPa, T=5.2-5.8 FTU, PC=11,040-11,670/mL.

Highest particle removal efficiency by filtration was obtained with a recirculation ratio of 5%, and efficiency slightly decreased with increasing recirculation ratio. This could be caused by the introduction of more bubbles in the DAF unit at increased recirculation ratios, increasing the chance that some of them are carried over with the DAF effluent and onto the filter. There, the bubbles may disturb the filter pore structure and contribute to the passage of particles through it.
5.3.6 Filtration efficiency and the MFI (Modified Fouling Index)

DAF effluent quality generally had a pronouncedly positive effect on the filter effluent quality, but the sedimentation + filtration treatment led to slightly higher overall removal efficiency. The turbidity and particle removal efficiency of the filtration step following DAF under optimal pilot plant conditions (7 g Fe(III)/m³, two step flocculation 1ₜ₁=18.2 min, 1ₜ₂=30 s, R=7%, P=500 kPa, without coagulant aid) were 96.9-97.3% and 97.4-98.8% respectively, compared to the full-scale sedimentation + filtration average removal efficiency of 98.6 and 99.7%, respectively. The residual iron in the former case was 0.08-0.17 g Fe_{total}/m³.

Recharge of the aquifer with treated water as practiced by WRK III leads to the use of the MFI as a major effluent quality parameter. Our attempts to link MFI, turbidity and residual iron for the full-scale plant proved unsuccessful (Fig. 5.6); it proved partly successful to establish a correlation link between filtrate particle count and turbidity [12]. The difference in particle removal efficiency between the pilot plant and the full-scale treatment options was even more pronounced with respect to the MFI. The full-scale filtrate MFI values during the 1995 research period were within the 5-26 s/L² range (mean value of 8.83 s/L²), and for the 1996 research period within the 5-12 s/L² range (mean value of 7.2 s/L²). Pilot scale filtrate MFI values for the 1995 research period were 46.6-97.8 s/L², the lower value being associated with an unusual low coagulation pH of 6.35. Longer term filter operation with the use of Wisprofloc-P coagulant aid resulted in drop of the MFI value from the initial 97.8 to 40.5 s/L² in six hours, however, accompanied by rapid filter clogging. In the case of a 7 g Fe(III)/m³ dose the MFI value was 95±5 s/L². These high values could be attributed predominantly to the relatively high DAF residual iron.

Further optimisation of the agglomeration phase by applying a combination of a higher coagulant dose (>7 g Fe(III)/m³) and cationic polyelectrolyte Superfloc C-573 led to a reduction of the MFI value. A combination of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid resulted in increased DAF efficiency (turbidity removal 93.6% and particle removal 98.6%, compared to efficiency after sedimentation of 96.7% and 97.7%, respectively). This had a positive impact on the filter efficiency, resulting in turbidity removal efficiency of 98.9% and particle removal efficiency of 99.8%; both results were better than those of the full-scale plant average. Both after DAF and filtration, the residual iron was lower than usual (0.97 and 0.08 g Fe(total)/m³, respectively), suggesting that coagulation and flocculation were more efficient. The corresponding MFI value of the filtrate was 19.1 s/L², in the range of the full-scale plant MFI values for this part of the year (1995).

During the experiments (September-October, 1996), the pilot filter lowered the residual manganese below the 50 μg/L MAC (in the range of 35 μg/L), thus overcoming one of its potential limitations. However, the high particle and turbidity filter removal efficiency was not accompanied by a reduction of the MFI. The 1996 pilot plant MFI values were again >50 s/L² and were higher than the full-scale filtration 7.2 s/L² MFI mean value for this period of the year. Although the filter pore size of the MFI measurement apparatus was 0.45 μm, a large part of the colloidal MnO₂ and the organo-iron complexes was retained on the filter. This resulted in a characteristic brown colour of the deposit and high MFI values.

Unfortunately, the effect of ozone conditioning on the filtrate MFI value could not be assessed. However, based on model water experiments positive results were expected, and the MFI is expected to further decrease towards the prescribed 5 s/L² value. This effect should be the result
of improved particle removal efficiency and possibly lower coagulant dose requirements (Chapter 4). On the other hand, KMnO₄ conditioning improved removal of particles >2.75 μm, however, the residual Mn and Fe, although below the prescribed limit of 50 μg/L and 200 μg/L respectively, still resulted in comparatively high MFI values >50 s/L².

5.4 CONCLUSIONS

Pilot plant investigations conducted with reservoir water that was characterised by a seasonal cyanobacteria bloom (of mainly *Microcystis aeruginosa*) indicated that the acceptable coagulant dose for DAF related to maximised algal removal was two to three times lower than the one applied in the full-scale sedimentation (7-12 g Fe(III)/m³ compared to 20-24 g Fe(III) + 0.2-0.5 Wisprofloc-P/m³). The DAF removal efficiency (before filtration) was somewhat lower in terms of turbidity removal and residual iron content, probably due to some degree of (partial) preferential complexation of the iron by the organic matter into difficult to remove organo-iron complexes (<1 μm), and hence a limited availability of coagulant for destabilisation. The incomplete coagulation occurring at the lower coagulant doses applied prior to DAF, especially with regard to the high NOM/DOC concentrations, and the generally lower efficiency of DAF in the removal of colloidal particles, are suggested responsible for the lower efficiency of the DAF + filtration, compared to the sedimentation + filtration treatment option.

However, the primary task of this study being particles (algae) removal (>1 μm), DAF was found very efficient and appropriate even at these relatively low coagulant doses. The mean DAF particle removal efficiency (>2.75 μm) for a coagulant dose of 7 g Fe(III)/m³ was 94.5%, as compared to 97.3% for sedimentation with 20 g Fe(III) + 0.2 Wisprofloc-P/m³. For a coagulant dose of 10 g Fe(III)/m³ the DAF particle removal efficiency was higher than the one achieved by the sedimentation with a combination of 24 g Fe(III) + 0.5 Wisprofloc-P/m³ (i.e. 96.3% and 95.9%).

The highest turbidity and particle removal efficiency was achieved at the lowest tested pH 6.35 (93.2 and 97.5%, respectively), suggesting the aiding effect of adsorption coagulation to the otherwise dominant sweep coagulation. Electrophoretic mobility measurements did not confirm complete particle charge neutralisation. The turbidity and particle removal efficiency decreased with pH increase (to pH 7 and 8), falling bellow the 90% value for pH 9, possibly related to precipitation of calcite particles.

Floculation times longer than 15 minutes were found necessary, and removal efficiency was insensitive to the floculation energy input (G value). The particle removal efficiency slightly decreased (from 96.6 to 94.5%) with increase of the G value from 10 to 70 s⁻¹ (30 and 50 s⁻¹ were also tested) while turbidity removal efficiency did not follow the same trend, reaching its ‘optimum’ at G=50 s⁻¹ (89.9%). The results suggest that the heterodisperse curvilinear floculation model for turbulent floculation could be applicable; this model assumes that the G value has little effect compared to the rectilinear model.

No significant improvement of the DAF effluent quality was observed for the combination of the coagulant dose of 7 g Fe(III)/m³ with cationic coagulant aid (organic or synthetic) in the dose range of 0.1-0.7 g/m³. This coagulant dosing was accompanied by only a slight particle surface charge decrease compared to the charge neutralisation that occurred in the experiments with model water, possibly influenced by the high NOM content.
The positive effect of ozone and potassium permanganate conditioning on the removal of particles (algae) by DAF, were demonstrated on bench-scale experiments with model water for the first, and on bench-scale and pilot plant scale for the second. Due to technical limitations of the pilot plant the efficiency of the first could not be comprehensively tested in the pilot plant. Results showed that the relatively low ozone dosages (in the range of 0.2 g O$_2$/g TOC or 1.2 g O$_3$/m$^3$) which significantly improved DAF process efficiency (by 40-50%) in the bench-scale experiments, resulted at pH 7 in bromate levels below the WHO provisional guideline value of 25 μg/L and approached the European guideline of 10 μg/L.

KMnO$_4$ conditioning at a dosage of 1 g/m$^3$ tended to raise DAF process efficiency, especially with respect to particle removal (97.5% mean particle removal of particles >2.75 μm, as compared to 96.3% in case of no KMnO$_4$ conditioning). The particle removal efficiency achieved by KMnO$_4$ conditioning and coagulant aid Superfloc C-573 use (dose ≥0.5 g/m$^3$) tended to further increase DAF efficiency typically by 5% (98.6% mean particle removal efficiency of particles >2.75 μm); this treatment option was statistically significantly more efficient than that of the full-scale sedimentation option. The residual Mn of the DAF process mode after filtration was below the 50 μg/L MAC (approximately 35 μg/L), while residual Fe$_{total}$ was also below the 200 μg/L MAC.

The variation of the recirculation ratio (5, 7 or 10%) had a minor effect on DAF turbidity and particle removal efficiency; slightly better results were obtained for the recirculation ratio of 7% (typically 1-2%). On the other hand, the filtration particle removal efficiency for the 5% recirculation ratio was slightly better (1-2%) than for the other values, possibly due to the reduced chance of filter pore structure disturbances from bubbles, which is related to the lower bubbles concentration at this recirculation ratio and decrease of the opportunity of their carry over onto the filters.

The pilot plant filter removal efficiency of particles and turbidity was slightly lower than that of the full-scale filters. This is related to the incomplete coagulation of the NOM and the lower efficiency of the DAF in the removal of the submicron particles, thus subjecting the filter in the DAF + filtration option to higher loads of colloidal matter. However, it should be taken into account that the full-scale plant results had been positively influenced by the fact that the filters were operated at half of their design capacity. The full-scale plant experienced difficulties in attaining the stringent MFI guideline of 5 s/L$^2$, especially during periods of algae blooms. Optimisation of the coagulation and DAF by increasing the coagulant dose to ≥15 g Fe(III)/m$^3$ in combination with ≥0.5 g Superfloc C-573 coagulant aid tended to outperform the sedimentation in terms of particle removal (≥2.75 μm), whilst resulting in comparable turbidity removal. The MFI value accomplished in the filtrate was below 20 s/L$^2$. Further optimisation of the coagulation + DAF + filtration scheme, offers a good prospect for treating the algae laden WRK III reservoir water. Further research attention for ozone application in WRK III circumstances emerges from the possible improvement of the resultant MFI values due to expected ozone induced particle removal efficiency improvement, coupled to the expected improvement of organic matter removal (including pesticides) by the GAC filtration. On the other hand, the count of particles in the <1 μm range suggested that MnO$_2$ and organo-iron complexes are the main contributors to the corresponding high MFI values (≥50 s/L$^2$) in case of KMnO$_4$, conditioning, asking for further optimisation of the filtration step in order to maximise the positive effects of the permanganate induced increase of DAF removal efficiency of particles in the algal size range.
REFERENCES


Chapter 6

THE ROLE OF FLOC SIZE AND DENSITY IN DISSOLVED AIR FLOTATION AND SEDIMENTATION

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-Parts of this chapter were published by A. Vlaški, A.N. van Breemen and G.J. Alaerts in (1997) Water Science and Technology, 36, 4, pp. 177-189.
ABSTRACT: Sedimentation and dissolved air flotation (DAF) were studied for particle removal, in particular of the single cells form of the cyanobacterium *Microcystis aeruginosa*. This cyanobacterium species is considered a suitable representative of algae and particles of the problematic size range (3-10 μm) in the assessment of removal efficiency. The agglomeration (coagulation/flocculation) phase was proven to determine the down-stream process efficiency. Relevant process parameters were studied on a bench-scale (using model water) and pilot plant scale (using reservoir water), including the influence of coagulant dose (FeCl₃), coagulation pH, flocculation time, energy input (G value), single stage versus tapered flocculation, and application of cationic polyelectrolyte as coagulant aid. The process efficiency was interpreted in function of the preceding agglomeration (coagulation/flocculation) phase and the obtained particle (floc) size distributions. The particle (floc) size - density relationship was addressed.

6.1 INTRODUCTION

The algal morphology and physiology have been reported to influence the treatment efficiency of algae laden water in various ways [1]. In principle, algae can be regarded as particles whose stability is due to: (i) electrostatic surface charge which is negative for pH 2.5-11.5, (ii) steric effects due to water bound on cell surface, to adsorbed macromolecules or extracellular organic matter (EOM) onto the cell [2, 3]; (iii) morphology and extremities, and (iv) motility [1, 4]. Compared to other suspended particles of inorganic nature and similar stability algae have the peculiarity that they are living matter comprised of numerous species with different morphological and physiological characteristics that may affect charge phenomena and steric behaviour, such as: size, shape, motility, cell wall and EOM composition, etc. For example, flagellated *Rhodomonas* spp. have been noted to escape from floc material because of their motility [4]. Therefore, no single treatment is equally effective for the removal of all species.

The single cell *Microcystis aeruginosa* size of 3-10 μm, its round shape and surface characteristics contribute to its persistent occurrence in filtrate water in many surface water treatment plants, even though all other quality criteria have been fulfilled [5]. It is considered to be among the most widespread algal species occurring in water reservoirs, as well as among the species that are most difficult to remove in water treatment (Chapter 1). This makes it a suitable reference particle to study efficiency of removal of algae or other classes of microorganisms of comparable size such as *Cryptosporidium parvum* and *Giardia lamblia*.

In the treatment line, the agglomeration (coagulation/flocculation) phase is typically the most critical to achieve overall efficient removal of algae (Chapters 3). It can be enhanced by the application of polyelectrolytes as coagulant aids and/or conditioning of the algae (e.g. by application of chemical oxidants such as ozone or KMnO₄) (Chapters 4 and 5). Physical pre-treatment (microstraining) can reduce a substantial share of the algal load, especially the larger size colonial and filamentous species. Optimisation of the subsequent solid-liquid separation process is essential for algal removal (Chapters 3, 4 and 5). The commonly applied separation processes are either plain or lamellar sedimentation, or dissolved air flotation (DAF), followed by rapid sand filtration. The destabilisation by the coagulation and the consequent flocculation of particles, as well as eventual polyelectrolyte and/or conditioner application, define the resulting particle (floc) size distribution. The particle charge, floc size, floc density, and the relation between floc size and floc density play decisive roles in the down-stream processes.
Previous particle size analysis research with relatively clean model water (polystyrene particles with diameter $d=0.87$ $\mu$m in distilled water [6], or kaolin particles with diameter $d=1.88$ $\mu$m [7] in tap water buffered with 100 mg NaHCO$_3$), indicated that the particle size distribution after coagulation/flocculation with Al(III) or Fe(III) salts in a dose range of 3-5 mg/L was most pronounced in the <100 $\mu$m size range. In the former case, floc growth continued until steady state (no change of floc dimensions) was achieved, as a function of the shear rate ($G$ value) and coagulant concentration. Increased coagulant concentration at constant $G$ value produced larger and more open floc structures. Higher coagulant concentrations at low $G$ values resulted in increased floc strength, while increasing $G$ for the higher coagulant doses resulted in increased amount of floc breakage (more significant than for the lower doses) into smaller and more compact floc structures [6]. Pilot plant DAF research with water from the Göta River in Gothenburg [8], Sweden defined the particle size range of 10 $\mu$m as the most significant and responsible for the high DAF efficiency after coagulation/flocculation with 5.3 mg Fe(III)/L, and with 5 or 20 min flocculation time at $G=30-70$ s$^{-1}$. This is in agreement with the conceptual DAF kinetic model of Edzwald et al. [3, 9, 10], while flocs of size in the range of 100 $\mu$m and larger are advised for sedimentation. On the other hand, Fukushima et al. [11] state that floc size in water treatment is in the range $10^{-1}$ - $10^{3}$ $\mu$m and that the production of larger flocs should be the target in a DAF based treatment, since large flocs have a much higher collision efficiency (proportional to the third power of the collision radius). Their arguments are based on water from a diluted kraft pulp black liquor with colour of 50 Units and to which 5 mg Al(III)/L coagulant were applied at pH 6.7. Under such conditions 80% of the particles was of size <500 $\mu$m.

The existing data diversity regarding the water treatment relevant particle (floc) size may partly arise from: (i) diversity of applied particle size determination techniques and absence of a standardised measuring procedure, (ii) susceptibility of some particles, especially flocs to structural changes due to the application of often inappropriate measurement techniques (e.g. the use of flow through counters in which high shear may disturb the aggregates structure), and (iii) different raw water quality characteristics (coagulation pH, temperature, initial particulate, colloidal and dissolved inorganic and organic matter concentration and composition, etc.), which can influence the obtained particle size distribution.

Organic or inorganic polyelectrolyte coagulant aids of cationic, non-ionic or anionic nature have been applied in sedimentation in numerous cases, especially at low initial particle concentrations. On the other hand, experiences with the use of polyelectrolytes as coagulant aids in DAF are controversial with respect to obtained benefits [12, 13]. In the Netherlands only one non-ionic organic, and one anionic organic (starch based) polyelectrolytes are in use, although previous research showed that synthetic cationic polyelectrolytes can be more efficient [14]. Their impact on the process efficiency depends on their charge and molecular weight characteristics, and is asserted through effects on the surface charge of the algae, as well as the obtained floc size distribution [15] (Chapters 3, 4 and 5).

The application of ozone and KMnO$_4$ as algae conditioners has been associated with spontaneous microflocculation, even before the addition of coagulant [16, 17, 18, 19]. However, ozone has also been found to cause an opposite effect resulting in an increase of the smaller size particle fraction [20, 21], as well as decrease of overall particle volume and mass and lower filter loading [22]. Both ozone and KMnO$_4$ have been associated with the creation of stress conditions for the algae, resulting in EOM and IOM release, which then act as coagulant aids and promote
spontaneous microfloculation [16], (Chapters 4 and 5).

The situation with respect to dominant particle (floc) sizes in treatment becomes more complicated if the submicron particle size range is considered, since it is most often determining the coagulation/floculation efficiency (Chapter 5). In addition to the spontaneous microfloculation effect, ozone induces the formation of colloidal matter from dissolved organic matter and enhances its subsequent removal [16, 17], however, affecting the coagulation and floculation process and the resulting particle size distribution. On the other hand, an important aspect of permanganate conditioning is the effluents quality is terms of residual Mn. This pertains to the dissolved permanganate, as well as to the colloidal and (presumably) filterable MnO2 manganese. Strictly avoiding overdosing and permanganate reduction by Na2SO3 are two possible strategies to prevent dissolved Mn residuals [18, 19] (Chapter 4). Filtration is able to reduce the most substantial part of the colloidal Mn fraction [18, 19]. On the other hand, MnO2 manganese and organo-iron complexes were suggested to be partly responsible for the significantly higher DAF effluent turbidity and high filter effluent MFI, compared to the sedimentation based treatment (Chapter 5). Nevertheless, it was also reported that the combined action of permanganate conditioning, and iron and cationic polyelectrolyte coagulation resulted in improved DAF efficiency and low effluent Fe and Mn residuals.

The present study addresses critical aspects of the agglomeration phase in advance of the DAF and sedimentation separation processes. It intends to quantify particle size frequency and particle volume distributions before and after the coagulation/floculation step, and after the down-stream DAF or sedimentation. This is done under different process conditions, including varied coagulant dose, coagulation pH, floculation velocity gradient and time, tapered versus single stage floculation, as well as for different treatment options, including the application of Fe(III) coagulant alone or in combination with cationic polyelectrolyte coagulant aid, and ozone or KMnO4 conditioning. This information would be used to interpret overall treatment performance, and identify the key factors in the process kinetics.

6.2 MATERIALS AND METHODS

6.2.1 Laboratory experiments with model water

The laboratory experimental set-up consisted of a batch-wise jar test apparatus with incorporated DAF facilities (Chapter 3 and 4). For both the sedimentation and the DAF modes of operation, the standard experimental procedure included coagulation at pH 8, temperature 20\degree C and a G value of 1,000 s\(^{-1}\) for 30 s. Other coagulation pH conditions were also tested for DAF (pH 6, 7, 8, and 9); the desired coagulation pH was achieved by adding HCl or NaOH, in amounts determined previously by titration. Periodical check-ups showed that the pH remained stable throughout the experiments. The floculation G and floculation time t were varied \((G=10, 30, 50, 70, 100 \text{ and } 120 \text{ s}^{-1} \text{ and } t=5, 15, 25, 30 \text{ and } 35 \text{ min})\). The coagulant (FeCl\(_3\) \cdot 6H\(_2\)O) doses were 0 - 15 mg Fe(III)/L, while the cationic polyelectrolyte (Superfloc C-573) doses were in the range of 0 - 1.5 mg Superfloc C-573/L for DAF and 0 - 3 mg Superfloc C-573/L for sedimentation. The rationale behind the dose range of polyelectrolyte was to approximately cover the range which corresponds to one tenth of the optimal Fe coagulant dose. The sedimentation time \(t_s\) was varied \((t_s=10, 20, 30, 45, 60 \text{ and } 90 \text{ min})\), while for DAF different recirculation ratios
R (R=5, 7 and 10%) and saturator pressures P (P=500, 600 and 700 kPa) were tested.

Ozone was used as an algae conditioner in the context of improving down-stream DAF efficiency. For ozone production, the Trailigaz LABO LO, France, ozone generator was used (Chapter 5, Fig. 5.12). Ozone was produced under standard ozone generator conditions of 220 V, 0.6 A, and 0.6-0.7 bar pressure. The ozone dosage (transferred ozone) was derived from the ozonation time which was varied from 1-4.5 min (Chapter 4). The pH of the raw (model) water subject to ozonation was previously set to 7.5 by HCl addition. A 5.5 L ozone resistant glass jar was used as a batch ozone reactor. The time gap between ozonation and subsequent coagulation and flocculation was kept at 2 min. The pH change after ozonation was 7.5 ± 0.2 and it served as coagulation pH without additional corrections. Ozone was applied in combination with the previously determined optimal coagulant dose for a concentration of ≈10,000 cells/mL of *M. aeruginosa* (3 mg Fe(III)/L). The cationic polyelectrolyte Superfloc C-573 was tested as a sole coagulant (0.3-1.0 mg/L), or as a coagulant aid (0.1-1.0 mg/L) to Fe(III) coagulant, combined with a low ozone dose of 0.2 mg O₃/mg C (0.58 mg O₃/L).

For permanganate conditioning experiments a 0.0057 M stock solution was prepared at weekly intervals. The applied permanganate dose ranged from 0.1-2.0 mg KMnO₄/L, while the pH was previously set at 8. The permanganate was applied at a G value of 400 s⁻¹ for a period of 1 min, followed by 30 min of slow mixing at a G value of 10 s⁻¹. It was combined with a previously optimised Fe(III) coagulant dose at coagulation pH 8.

The investigated cyanobacterium species was a semi-continuously laboratory cultured, single-cells form of *M. aeruginosa*. The model water originated from the Biesbosch storage reservoirs, the Netherlands, and was spiked with the cyanobacteria to achieve an initial concentration of ≈10,000 or 20,000 ± cells/mL. The experiments did not include a final filtration step.

### 6.2.2 Pilot plant experiments

The pilot plant research was conducted on the premises of the Princess Juliana treatment plant (WRK III) situated on the shores of the IJssel Lake in Andijk, the Netherlands (Chapter 5). The raw water used in the experimental work was reservoir water previously subject to microstraining over a 35 μm mesh. The period of the research (late summer, early autumn) coincided with a bloom of *M. aeruginosa*, a common species in the IJssel Lake in this period of the year. The DAF pilot plant investigations were carried out with a commercial (Purac, Sweden) pilot plant installation (Q_max = 13 m³/h). The unit itself comprised a 1 m³ stainless steel tank with four needle valves located at the bottom of the inlet for the recycled water stream introduction. Coagulation occurred in a Kenics-type in-line mixer (Purac, Sweden); one, two or three-stage flocculation could be applied with variable speed flocculation paddles. An automated system regulated the pumps, the saturation and the recycled flow. The experiments did not include a final filtration step.

Fe₂(SO₄)₃ · 9H₂O was used as coagulant in a dosage range of 0-20 g Fe(III)/m³. pH in coagulation was set at pH 8 using Ca(OH)₂, as in the full-scale WRK III process. The synthetic cationic polyelectrolyte Superfloc C-573 was tested as a coagulant aid in the concentration range of 0.1-0.7 g/m³. The Kenics static mixer was used for the rapid mix with a calculated G value of ≈3,500 s⁻¹ for a flow of 4.6 m³/h. This flow was applied in the DAF pilot plant in order to
avoid carry-over of bubbles into its effluent and onto the filters, a common occurrence in case of higher flows. Different flocculation time, energy input (G value) and flocculation sequence (one-, two- and three-stage flocculation) were tested; the values were partly dictated by the technical provisions of the pilot plant. The recirculation ratio R in the DAF unit was set at R=5, 7 and 10%, while the saturator pressure P was 500 kPa. The water temperature over the experimental period decreased from 16.7°C to 10.1°C in 1995, and from 16.4 °C to 12.9 °C in 1996.

Because of disproportion between the pilot plant flow (Q=4.6 m³/h) and the continuous-flow ozone reactor (Q_{max}=1.14 m³/h), only a limited number of pilot plant ozone conditioning experiments was carried out, assessing primarily the issue of bromate formation (Chapter 4). Potassium permanganate (0.0021M working solution) was dosed immediately before pH correction and coagulant addition, allowing for very short contact times (<1 s) before coagulation and flocculation.

Model water experiments were intended to simulate relatively “clean” water circumstances and provide conditions in which the assessment of the removal of the spiked algae would be affected to a limited degree by other water quality parameters (i.e. the presence of larger quantities of other suspended, colloidal and dissolved matter of inorganic or organic origin). Thus, the algae were the most significant factor determining the optimal process conditions and the achieved efficiency. These experiments were used to optimise DAF and sedimentation process conditions on bench-scale and gain deeper insight into the governing process mechanisms, which was to serve as basis for the DAF pilot plant optimisation. On the other hand, the WRK III reservoir (Chapter 5) provided for the “real” water conditions in which the naturally occurring cyanobacteria bloom of *M. aeruginosa* was coupled with other water quality factors of importance for process optimisation and of influence on process efficiency (i.e. temperature, NOM concentration and composition, inorganic colloidal and particulate matter, etc.). These results were then compared to the results achieved by the full scale WRK III sedimentation based treatment. Particle size and density relations emerging from both experimental modes are used to highlight important process phenomena.

### 6.2.3 Analytical techniques

Process evaluation was based on turbidity (Sigrist L-65, Switzerland), particle (algae) count measurements of particles in the size range 2.75-150 µm (HIAC-Royco PC-320, USA) and residual coagulant concentration (Fe_{total}). These measurements were compounded by inverted microscope count (M40-Wild Leitz, Switzerland), and electrophoretic mobility (Tom Lindström AB-Repar). Other particle analysis techniques included particle count of particles in the size range of 0.3-5 µm (Particle Measuring Systems Inc./Liquid Batch Sampler LBS-100, and the Microlaser Particle Spectrometer, Boulder, Co., USA) and computer image analysis (Mini-Magiscan, IAS 25/1V25 Joyce-Loeb Ltd., UK). The use of the former technique was limited to a number of KMnO₄ conditioning experiments and the assessment of the colloidal MnO₂ and Fe residuals involvement in the overall DAF effluent quality.

The computer image analysis results are presented in the form of particle size frequency and volume distributions. The frequency and volume distributions represent the number and the
volume of recorded particle size range. For this purpose the recorded particles and/or floc material were approximated to spheres and presented in size ranges of 10 µm, from 0-200 µm. Particles >200 µm were also recorded (by image analysis and visually), in particular after flocculation; their frequency increase was associated with higher coagulant doses, lower flocculation G values and longer flocculation times, as well as with the raw water quality: larger flocs were observed in the reservoir water than in the model water experiments. However, large flocs represented only a small percentage of the overall particle concentration, especially for the "clean" model water circumstances (by concentration <2.5% of particles (floc) were of size >100 µm for a dose range of 0-10 mg Fe(III)/L, pH 8, G=70 s⁻¹ and t=10 min). The removal of large particles by the solid-liquid separation process (DAF or sedimentation) was complete, while the smaller particles proved to be more problematic in this respect. Thus, the adopted size limit in the discussion of the results is 200 µm, while the particle size of 50 µm, which is roughly the size limit of visually observable aggregates, was tentatively adopted as the size dividing the smaller from the larger particle size range.

The image analyses were performed on fresh samples, as well as on photographs of samples. Photo analysis was preferred over fresh sample analysis, since it enabled registration of representative situations at different spots along the treatment line, without the potential danger of disturbing the process or the quality of the sample [23]. For this purpose, a specially devised flat photo cell was connected at different locations of the jar test apparatus and the pilot plant unit, and samples were photographed before and after flocculation, and after particle removal. Special care was taken to avoid break-up of particle agglomerates (flocs) during the passage of the sample from the jar test unit to the photo cell, by allowing low flow velocities adjusted through a system of valves. In case of DAF, the released air bubbles were also photographed and analysed. Professional high resolution black-and-white film AGFA 25 or Kodak TMAX 100 was used for the purpose, while forced development was applied for film processing. 30-100 fields, or more than 500 particles of each film shot were processed and analysed, using a ccd-camera (604*288 pixels) mounted to a Nikon Optiphot microscope (at 40x magnification). The minimum detectable size under these circumstances was 1.9 µm. The software package Genias25 developed by Joyce-Loebl (UK) was used for data processing.

The computer image analysis is subject to a measurement error which varies with the size of the recorded particle and the applied magnification. Previous work [23] showed that the smaller the particle and the magnification, the larger the measuring error. This is due to the fact that the particle area used for calculations of the particle diameter is measured as the full area of all the computer screen pixels over which the particle image is spread, even if the pixels at the edge of the image are not fully covered. In the case of 40x magnification (pixel size of 1.9x1.9 µm), we showed that for an 8 µm size *M. aeruginosa* cell the calculated cell diameter was 25-50% larger than the actual cell dimension. This explains the particle frequency peak of the raw (model) water which occurred at the 10-20 µm, instead of at the expected 0-10 µm range (Fig. 6.2 and 6.3). For larger particles (flocs>10 µm) the measurement error led to up to 10% higher values than the actual sizes. To verify the reproducibility of the applied analytical technique, multiple shots of the same sample were analysed regularly.

Particle size distributions departed strongly from Gaussian shapes. Statistical comparison of data on particle size frequency distributions from experiments that were performed under identical conditions was carried out using the chi-square test. Testing for the hypothesis that the obtained
particle size distributions were identical resulted in a probability level of \( p = 0.999 \), confirming highly comparable particle size distributions and hence high experimental reproducibility.

6.3 RESULTS AND DISCUSSION

6.3.1 Coagulant dose

The settling characteristics of a flocculent suspension depend on floc size, floc density, water temperature [24] and on initial particle number concentration [25]. The influence of the coagulant dose on the overall performance of the sedimentation based process is presented in Fig. 6.1 in the form of particle volume distribution at initial algal concentration of 10,000 cells/mL and for coagulant dose of 6 mg Fe(III)/L and 15 mg Fe(III)/L. The flocculation step for the 6 mg Fe(III)/L coagulant dose resulted in the production of a substantial volume of flocs in the larger particle size range (>50 \( \mu \)m); the 15 mg Fe(III)/L dose contributed even more significantly to this particle size range, whilst maintaining the generation of a large volume composed of the smaller particles (<50 \( \mu \)m).

![Graph showing particle size distribution](image)

**Fig. 6.1** Particle volume distribution of raw water, and before and after sedimentation at coagulant dose of 6 versus 15 mg Fe(III)/L (bench-scale), pH 8, flocculation \( G_f = 30 \) s\(^{-1} \) and \( t_f = 30 \) min, and sedimentation \( t_s = 60 \) min.

The optimal coagulant dose for sedimentation in case of an algal concentration of 10,000 cells/mL was 10 mg Fe(III)/L, three times higher than that for DAF (3 mg Fe(III)/L) (Chapter 3). Fig. 6.2 depicts particle (floc) size frequency distributions after flocculation and after DAF at the algal concentration of 20,000 cells/mL for the different coagulant doses of 1 (a), 3 (b), 5 (c) and 10 mg Fe(III)/L (d). The intermediate dose of 5 mg Fe(III)/L was most efficient (also when expressed as turbidity and particle count measurements), suggesting an approximately proportional stoichiometry between optimal coagulant dose and initial particle concentration [1, 26] (Chapter 4). The dose of 1 mg Fe(III)/L was inadequate for sufficient particle destabilisation and significant floc formation, which would shift the particle (floc) size distribution and result in a particle size distribution favouring DAF. The increase in the frequency in the smaller particle size range (<50 \( \mu \)m) due to iron flocs precipitation [8] and the small effect on the larger particle size range (>50 \( \mu \)m)
μm) resulted in poor DAF performance. Thus, the sweep coagulation conditions at this low coagulant dose were not fully appropriate resulting in inefficient flocculation and particle removal by DAF, coupled to high residual coagulant concentration (only ≈60% of the Fe coagulant dose was removed). HIAC particle count measurements of acidified effluent showed that the count at the higher coagulant doses can consist up to 15% of the residual coagulant.

![Graphs showing particle size frequency distribution before and after DAF at different coagulant doses](image)

**Fig. 6.2** Particle size frequency distribution before and after DAF at different coagulant dose (bench scale): (a) 1 mg Fe(III)/L, (b) 3 mg Fe(III)/L, (c) 5 mg Fe(III)/L and (d) 10 mg Fe(III)/L. Conditions: pH 8, G_f=70 s⁻¹, t_f=10 min, R=5%, P=5 bar. Notation: + raw water, △ water after flocculation, and ■ after DAF.

Raising the dose to 3 mg Fe(III)/L enhanced the formation of particles in the larger size range (>50 μm) and resulted in improved DAF removal efficiency. At the most efficient particle removal dose of 5 mg Fe(III)/L, both the frequencies of particles in the smaller and the larger particle size ranges were increased by flocculation. The corresponding particle volume distribution (not presented) of the flocculated water at this coagulant dose, showed that the recorded increase of particle frequency in the smaller size range, corresponded to a decrease in the particle volume for this range (both relative to the raw water). This may be ascribed to a change in the nature of the particles of size <50 μm before and after flocculation: iron micro-flocs taking the place of the
original algae which were flocculated and shifted to the larger size range. The 10 mg Fe(III)/L dose contributed to the <50 \mu m size range in a similar way as the 1 mg Fe(III)/L dose, but nevertheless resulted in better removal efficiency due to the floculation of algae into flocs of size >50 \mu m. In this set of bench-scale experiments with model water the particle fraction of particle size >100 \mu m contributed only up to 1% of the total particle amount, but corresponding high particle volumes (40-50% of total particle volume after floculation). In the pilot plant case, particles of larger size (up to 200 \mu m and larger) were present (Figs. 6.5 and 6.6), however, these were completely removed by the DAF treatment (data not shown).

6.3.2 Coagulation pH

The coagulation pH influences the extent and the rate of hydrolysis of metal coagulants, and it also determines the composition and surface charge of polymeric metal hydrolysis species [14]. The pH simultaneously controls the stoichiometry and kinetics of other chemical reactions, and influences the surface charge of algae and other particulate matter. The effect of coagulation pH on particle agglomeration and on overall removal efficiency after DAF is presented in Fig. 6.3.

Fig. 6.3 Particle size frequency distributions before and after DAF at different coagulation pH (bench-scale): (a) pH 6, (b) pH 7, (c) pH 8 and (d) pH 9. Other conditions: 10,000 cells/mL, 10 mg Fe(III)/L, G_r=70 s^{-1}, t_r =10 min, R=5%, P=500 kPa. Notation: + raw water, \Delta water after flocculation, and \times after DAF.
Image analysis data after flocculation show a more pronounced reduction in the smaller particle size range, and an increase in the larger size range at pH 6 (Fig. 6.3.a), compared to pH 7 and 8 (Figs. 6.3.b and 6.3.c). In all cases, at the low and the neutral pH, the coagulant dose tended to produce more large size aggregates which were efficiently removed by DAF. At the neutral pH of 7-8, particle agglomeration was likely to have been achieved solely through sweep coagulation [27] (Chapter 3). The surface charge of the destabilised colloidal and floc material remained negative. However, at pH 6 adsorption coagulation and charge neutralisation (verified by EM measurements, not presented) substantially contributed to particles destabilisation beside the dominant sweep coagulation. This almost doubled particle removal efficiency, suggesting that adsorption coagulation plays an important role in algae flocculation. The frequency increase at pH 9 (Fig. 6.3.d) of both the smaller and larger particles, may be ascribed to precipitation of CaCO₃ under alkaline conditions. Electrophoretic mobility measurements (data not shown) confirmed that algal charge neutralisation occurred at the low pH conditions (pH 6), which is in accordance with other research [15, 28]. The turbidity data and particle count measurements correlated with the image analysis results (data not shown). The charge neutralisation mechanism is also suggested to cause the higher removal efficiency of particles in the smaller particle size range (<50 μm) at pH 6, as the adsorption efficiency between neutralised particles and negatively charged air bubbles was higher [29].

6.3.3 Flocculation conditions

The agglomeration process which has already begun in the coagulation phase with the fast precipitation of metal coagulant species, continues during the flocculation phase under slow mixing. The optimal slow mixing intensity and period are a function of the down-stream process. These two parameters further influence the particle (floc) size distribution and density, and thus the down-stream process efficiency.

Floc size and flocculation energy input (G) were found by image analysis to be inversely proportional (Fig. 6.4).

![Graph showing particle volume distribution for different flocculation Gs (bench-scale). Conditions: pH 8, 3 mg Fe(III)/L, t_f=10 min.](image)
Jar test experiments at a low G value of 10 s\(^{-1}\) resulted in a floc volume distribution which led to highest DAF removal efficiency (Chapter 3), although flocs were of weaker structure compared to those generated at higher G values (as in the case of G=23 s\(^{-1}\)). Therefore, the statement [12, 15] that DAF requires high flocculation G in order to produce smaller, stronger and shear resistant flocs, may require adjustment. On the other hand, floc volume distributions obtained at flocculation G values of 10-30 s\(^{-1}\) favoured sedimentation (Fig. 6.1). It is therefore suggested that the floc density plays an equally important role as the floc size, yielding slightly better results at G=30 s\(^{-1}\), in combination with flocculation time \(\geq 30\) min (Chapter 3).

Image analysis data of reservoir water flocculated in pilot plant circumstances with G=10 and 50 s\(^{-1}\), are presented in Fig. 6.5. In this case, the inverse relation between floc size and flocculation energy input was less pronounced; an increase of flocculation G seemed necessary, possibly to provide more contact opportunities for the particulate matter in the \(<50\ \mu\text{m}\) size range. The reduction of the frequency (data not shown) of recorded particles in the range \(<50\ \mu\text{m}\) increased with increasing G. The extent of the reduction is less obvious on the presented cumulative particle volume graph (Fig. 6.5) due to the significantly smaller share of the small particles (\(<50\ \mu\text{m}\)) in the volume (about 10% of the total volume after flocculation). The flocculation G=50 s\(^{-1}\) value produced the best turbidity removal (89.9%), while the particle removal was comparable for all G values (\(\approx 95\%\)), slightly better at G=10\(^{-1}\) (96.6%).

![Cumulative particle size volume distribution for different flocculation G values](image)

**Fig. 6.5** Cumulative particle size volume distribution for different flocculation G values (pilot plant). Conditions: pH 8, 10 g Fe(III) + 0.3 g Superfloc C-573/m\(^3\), \(t=20\ \text{min}\), R=7%, P=500 kPa.

Similar to the jar test experiments with model water, the pilot plant experiments showed that tapered flocculation did not significantly improve overall DAF performance (Chapter 5). Particle volume distribution after each of the two stages of the applied tapered flocculation in pilot plant experiments showed that there was an increase in the volume of particles in the larger size range, on account of a decreasing volume of the smaller particles, as G decreased in the second flocculation step (Fig. 6.6). However, overall tapered flocculation had little impact on the final DAF effluent quality compared to that of the single-stage flocculation DAF at similar flocculation G and flocculation times. It is therefore suggested that in the case of DAF total flocculation time is more important than the tapering effect [9] (Chapter 5).
6.3.4 Polyelectrolyte as coagulant aid

The use of organic or inorganic coagulant aids of cationic, non-ionic or anionic nature has been known to sedimentation in numerous cases, especially at low initial particle concentrations. On the other hand, experiences with the use of polyelectrolytes as coagulant aids in DAF are controversial with respect to obtained benefits [12, 13]. In the Netherlands only one non-ionic organic, and one anionic organic (starch based) polyelectrolytes are approved, although previous research showed that synthetic cationic polymers can be more efficient [14]. Relatively low cationic polyelectrolyte (Superfloc C-573) doses of approximately one tenth of the optimal coagulant dose can substantially improve product water quality (Chapter 3). Particle removal efficiency (as measured by HIAC) for DAF of model water rose from 71% to 94% (at a dose of 0.5 mg Superfloc C-573/L), and for sedimentation from 88% to 99.5% (at a dose of 1.0 mg Superfloc C-573/L). This was accompanied by charge neutralisation of the particulate matter at a dose somewhat higher than the determined optimal one (Fig. 6.8), similar to what was found by other research [30]. Particle volume distributions of the flocculated model water with and without the addition of coagulant aid (Fig. 6.7) showed that agglomeration improved in the former case. It resulted in a more pronounced larger particle size fraction, on account of a reduction of the smaller particles fraction. Furthermore, an increase of the polyelectrolyte dose resulted in a decrease of the volume associated with the larger particle size fraction. This suggests that denser floc structures were formed at the higher polyelectrolyte dose; 0.5 mg Superfloc C-573/L favoured DAF, whereas the 1.0 mg/L favoured sedimentation.

![Cumulative particle volume distribution for tapered flocculation (pilot plant).](image)

Fig. 6.6 Cumulative particle volume distribution for tapered flocculation (pilot plant). 1st stage (S1): \( G_1 = 50 \text{ s}^{-1} \), \( t_1 = 18 \text{ min} \), 2nd stage (S2): \( G_2 = 30 \text{ s}^{-1} \), \( t_2 = 4 \text{ min} \), pH 8, 15 g Fe(III) + 0.5 g Superfloc C-573/m³.

Image analysis of reservoir water after flocculation confirmed these observations (Fig. 6.6). The concentration of particles in the 30-150 μm size range increases in case of application of 15 g Fe(III)/m³ only. This situation changes in case of combined application of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³ coagulant aid, resulting in denser floc structures, with slight increase of particles or flocs in the >150 μm range. In the case of the DAF pilot plant investigations, the
positive impact of the cationic polyelectrolyte was less pronounced than in the laboratory jar test experiments with model water. This improvement was accompanied by a slight surface charge decrease (from -1.29 to -0.88 μS/V/cm at coagulation pH 6.35, and from -0.84 to -0.78 μS/V/cm with 0.5 g/m³ cationic coagulant aid at coagulation pH 8, and with 7 g Fe(III)/m³ in both cases), as compared to the complete charge neutralisation which occurred in the model water experiments (Fig. 6.8). As discussed in Chapter 5, this suggests the importance of the NOM concentration and composition for the coagulation process.

**Fig. 6.7** Cumulative particle volume distribution for flocculation without and with polyelectrolyte Superfloc C-573 coagulant aid (bench-scale). Conditions: pH 8, 10 mg Fe(III)/L + Superfloc C-573, G_r=30 s⁻¹, t_f=30 min.

**Fig. 6.8** Electrophoretic mobility (EM) as a function of polyelectrolyte Superfloc C-573 coagulant aid dose for bench scale DAF (+) (3 mg Fe(III)/L, G_r=70 s⁻¹, t_f=10 min), and sedimentation (△) (10 mg Fe(III)/L, G_r=30 s⁻¹, t_f=30 min) with model water.
6.3.5 Ozone conditioning

The spontaneous microfloculation induced by ozone conditioning was discussed in Chapter 4 (Figs. 4.14 and 4.18). Here, the influence of different treatment options on the particle (volume) distribution is discussed: Fe(III) coagulant only treatment (Fig. 6.9), combined ozone and Fe(III) coagulant (Fig. 6.10), combined ozone, Fe(III) and Superfloc C-573 coagulant aid (6.11), and finally ozone and Superfloc C-573 as sole coagulant (Fig. 6.12).

![Particle volume distribution after different treatment stages in the case of treatment with Fe(III) coagulant only (bench-scale). Conditions: 3 mg Fe(III)/L, pH 7.5, G_f=10 s⁻¹, t_f=10 min, R=7%, P=500 kPa.](image)

Fig. 6.9

Fig. 6.9 indicates the efficient removal of the flocculated material and the absence of larger size particles in the flotate, however, the residuals in the lower particle size range were still considerable. The impact of the relatively low ozone dose of 0.2 mg O₂/mg C on the particle volume distribution can be observed by comparing the raw water particle distribution in Fig. 6.9 and the ozonated water particle distribution in Fig. 6.10; the latter was the 'raw water' that was further subjected to coagulation and flocculation. The impact of the 3 mg Fe(III)/L coagulant dose resulted in this case in more efficient particle coagulation and subsequent flocculation, as expressed in the more pronounced larger particle (floc) size fraction of the flocculated water. The EOM and IOM release are suggested to have eventually resulted in improved DAF particle removal efficiency, including that of the lower particle size ranges.

Similar to our previous experiences with coagulant aid (Chapter 4), the combined ozone, Fe(III) and Superfloc C-573 cationic polyelectrolyte treatment (Fig. 6.11) led to a denser floc structure. This phenomenon benefitted DAF efficiency, resulting in further improvement of the particle removal compared to the two previously discussed options. Particle count (HIAC) and turbidity measurements support these findings. On the other hand, the combination of ozone conditioning and 1 mg Superfloc C-573/L as sole coagulant did not yield different results from the ozonated sample prior to other treatment, suggesting that the relatively high polyelectrolyte dose resulted in comparatively denser floc formation. The combination of the 1 mg Superfloc C-573 with the 0.2 mg O₂/L resulted in comparably good DAF particle (HIAC) and turbidity removal efficiency.
Fig. 6.10  Particle volume distribution after different treatment stages in the case of combined ozone conditioning with 0.2 mg O₃/mg TOC and 3 mg Fe(III)/L coagulant treatment (bench-scale). Conditions: ozonation pH 7.5, coagulation pH 7.5 ±0.2, $G_f=10$ s⁻¹, $t_f=10$ min, $R=7\%$, $P=500$ kPa.

Fig. 6.11  Particle volume distribution after different treatment stages in the case of combined ozone conditioning with 0.2 mg O₃/mg TOC + 3 mg Fe(III)/L + 0.5 mg Superfloc C-573/L coagulant aid treatment (bench-scale). Conditions: ozonation pH 7.5, coagulation pH 7.5 ±0.2, $G_f=10$ s⁻¹, $t_f=10$ min, $R=7\%$, $P=500$ kPa.
Fig. 6.12  Particle volume distribution after different treatment stages in the case of combined ozone conditioning with 0.2 mg O₃/mg TOC + 1.0 mg Superfloc C-573/L coagulant treatment (bench-scale). Conditions: ozonation pH 7.5, coagulation pH 7.5 ±0.2, Gᵢ=10 s⁻¹, tᵢ=10 min, R=7%, P=500 kPa.

6.3.6 KMnO₄ conditioning

As discussed in Chapter 4, permanganate conditioning also resulted in spontaneous microfloculation, initiated again by phenomena related to EOM and IOM release, even before the application of the iron coagulant. The subsequent application of 5 mg Fe(III)/L resulted in further increase of particle volume both in the larger and the lower particle size fractions (Fig. 6.13). DAF experiments with model water resulted in statistically insignificant improvement of the particle removal efficiency due to permanganate conditioning (mean particle removal of 49% compared to 40% without permanganate conditioning). The overall relatively low particle removal efficiency in the case of permanganate conditioning (Fig. 4.28) was also observed in the experiment described in Fig. 6.13, especially in the lower particle size fraction. In Section 4.3.4 a hypothesis was offered to explain the unexpectedly poor efficiency of DAF in case of model water after permanganate conditioning, relating it to TOC/DOC concentration and composition.

Fig. 6.14. describes the particle size distributions (0.3-1μm) after the DAF and filtration in the pilot plant experiments, and for comparison purposes after the full-scale sedimentation and filtration (WRK III treatment plant in Andijk). The full-scale sedimentation (E) and filtration (F) plant was operated at a coagulant dose of 24 g Fe(III)/m³ and 0.5 g Wisprofloc-P/m³ cationic coagulant aid. The pilot plant results relate to DAF (A) and filtration (B) at coagulant doses of 15 g Fe(III)/m³ and 0.5 g Superfloc C-573/m³. The combination of conditioning with 0.96 g KMnO₄/m³ and coagulation with 15 g Fe(III)/m³ + 0.5 g Superfloc C-573/m³ is also presented for DAF (C) and filtration (D). The distributions show up to 100% more particles of the colloidal size <0.5 μm to remain after pilot plant DAF (A and C, C with KMnO₄ conditioning) than after full-scale sedimentation (E).
Fig. 6.13  Particle volume distribution after different treatment stages in the case of combined permanganate conditioning with 0.7 mg KMnO₄/L and 5 mg Fe(III)/L coagulant treatment (bench-scale). Conditions: KMnO₄ contact time 30 min, pH 8, Gₑ=70 s⁻¹, tₑ=15 min, R=7%, P=500 kPa.

<table>
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<th>TREATMENT</th>
<th>DAF</th>
<th>DAF+FILTER</th>
<th>KMnO₄ (mg/L)</th>
<th>Fe₃⁺ (mg/L)</th>
<th>C-573 (mg/L)</th>
<th>W-P (mg/L)</th>
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Fig. 6.14  Laser particle count in the colloidal size range (<1µm) for the DAF + filtration (pilot plant) in the case of Fe(III) coagulant and Superfloc C-573 coagulant aid treatment, and combined KMnO₄ conditioning, Fe(III) coagulant and Superfloc C-573 coagulant aid treatment, versus the full-scale WRK III plant with sedimentation + filtration (pilot plant MFI = 56.6 s/L²).
At the same time, Fe (in case of A) and Fe and Mn residuals (in case of C) (data not shown) were substantially higher than after sedimentation (E) which applied very high metal coagulant doses. This suggests that the lower metal coagulant dose used for DAF fails to remove the organo-Fe complexes and MnO₂ colloids well, as does the higher coagulant dose used for sedimentation. The rising slope of the distribution curves towards the smaller size particle region suggests possible higher involvement of colloidal particles <0.3 μm (lower size instrument limitation) in the resultant turbidity. The particle distribution after filtration in the case of combined Fe + polyelectrolyte coagulation (B) suggests that the residual Fe and the likely residual polyelectrolyte contributed to the relatively high effluent MFI. The permanganate conditioning tended to increase the DAF particle removal efficiency both for particles >2.75 μm (Fig. 5.27) and for submicron particles (C versus A). The same applies for the submicron particle size range of DAF + filtration (D versus B), which approaches that of the full-scale sedimentation + filtration submicron particle removal efficiency (E). Nevertheless, the total particle count in the size range of 0.3-1 μm is still by more than 30% higher for DAF + filtration than for sedimentation + filtration. The higher DAF + filtration effluent particle counts in the size range <0.3 μm, suggest that these particles were the source of the observed higher MFI as compared to those of the sedimentation + filtration treatment.

Finally, the sedimentation + filtration efficiency relied on high metal coagulant doses which can periodically reach up to 45 g Fe(III)/m³ combined with Wisprofloc-P as coagulant aid (up to 0.5 g Wisprofloc-P/m³). These high coagulant doses resulted in high overall floc volume concentration, more efficient co-precipitation of DOC, and possibly more efficient colloid destabilisation, resulting in efficient removal of initial particles, as well as lower coagulant residuals and MFI values.

6.3.7 Bubble size distribution

Bubbles influence DAF kinetics through their size distribution and their (negative) surface charge characteristics. Our theoretical model analysis has shown that for a given particle size distribution, process efficiency can be influenced if the bubble size distribution can be modified [31] (or see Chapter 7).

Variation of the saturator pressure P and recirculation ratio R resulted in different bubble size distribution (Fig. 6.15). The mean bubble size was 48-61 μm. The increase of R resulted in a higher bubble concentration and a ‘wider’ bubble size distribution (with a higher standard deviation) with 2-3 times more bubbles of size <40 μm and 30% fewer bubbles > 60 μm. An increase of P at constant R (data presented in Chapter 7) also shifted the bubble size distribution towards smaller bubble sizes that theoretically are more efficient, and reduced the standard deviation of the population. However, the overall DAF efficiency theoretically depends on the combination of the bubble and particle (floc) size distributions (Chapter 7). Our experimental work with model water showed that the combination of these bubble size distributions with different particle size distributions resulted in insignificant difference of DAF efficiency (Chapters 3, 5 and 7). It is concluded that under our typical conditions the high bubble concentration relative to the particle concentration (>1.9 μm) is an important determinant for DAF efficiency. Consequently, combinations of low to medium R and P (e.g., R=5-7% and P=500 kPa) suffice for obtaining high DAF efficiencies (see also Chapter 7).
Fig. 6.15 Bubble size distributions for a saturator pressure P=600 kPa and recirculation ratios of R=5, 7 and 10 % (bench-scale DAF jar test unit with model water, T=20°C, S=standard deviation).

6.3.8 Floc size - density relationship

The floc size - density relationship has been investigated among others by Boller and Kavanaugh [32]. In their attempt to model the headloss development in a granular media filter bed, they assumed that particle deposition in filters occurs in a manner similar to the phenomena occurring during the flocculation process. Flocculation is the process of aggregation of suspended and colloidal particles in water into larger agglomerates called flocs which are of a loose structure and entrap water as well. The mass of a floc $m_f [M]$ containing $N$ particulates of volume $V_p [L^3]$ and density $\rho_s [M/L^3]$ is given by:

$$m_f = N \cdot V_p \cdot \rho_s + V_w \cdot \rho_w$$  (1)

$V_w [L^3]$ being water volume in a floc and $\rho_w [M/L^3]$ being the density of water. The ratio between the floc mass $m_f$ and the floc volume $V_f [L^3]$ given by $V_f = V_w + N V_p$ expresses the suspended floc density (effective density) $\rho_{\text{fl}}$ as:

$$\rho_{\text{fl}} = \frac{m_f}{V_f} = \frac{(N \cdot V_p \cdot \rho_s + V_w \cdot \rho_w)}{(V_w + N \cdot V_p)}$$  (2)

By rearranging equation (2), the relative density of a floc ($p$) can be expressed as a ratio of the product of the aggregated number of primary particles ($N$) and their volume ($V_p$), and the obtained floc volume ($V_f$):

$$p = \frac{(\rho_{\text{fl}} - \rho_w)}{(\rho_s - \rho_w)} = \frac{N \cdot V_p}{V_f}$$  (3)
Boller and Kavanaugh also summarised the results of work of different authors [32] who assessed the floc size-density function and expressed it in a model equation relating the ratio between floc volume \( V_f \) and primary particles volume \( V_p \) as a function of the aggregated number of particles \( N \):

\[
\frac{V_f}{V_p} = a \cdot N^b
\]  

(4)

in which \( a \) and \( b \) are empirical dimensionless equation coefficients. Thus, referring to equation (3) and (4), the relative density of a floc can be expressed as:

\[
p = \frac{1}{a} \cdot N^{(1-b)}
\]  

(5)

The coefficients \( a \) and \( b \) have been theoretically derived by a number of authors whose assumptions are based on the aggregation of mono-disperse primary particles. The coefficient values differ slightly depending on the definition of floc volume and size. Assuming that the particle size distribution of the raw water sample containing the single cells \( M. \ aeruginosa \) may be treated as fairly mono-disperse, and approximating the floc volume with that of a sphere with the same silhouette surface area as the projected area of the floc as measured by computer image analysis, the model coefficients were chosen as: \( a=1 \) and \( b=1.305 \), based on work of Medalia (as discussed by Boller and Kavanaugh [32]).

Using volume distribution data obtained by image analysis of water before and after flocculation under different process conditions and eqs. (3) and (4) the flocs relative density \( p \) can be calculated for an \( M. \ aeruginosa \) flocculated suspension. Further use of equation (3) can yield the suspended floc density \( \rho_f \), which is significant for kinetic model calculations. The relative floc density calculated from the jar test results with model water at different coagulation (coagulant and polyelectrolyte doses) and flocculation conditions (G value) are presented in Fig. 6.16.

![Graph](image)

**Fig. 6.16** Relative floc density \( p \) (eqs 3 and 4) versus (mean) floc size (from computer image analysis) for different coagulation and flocculation conditions (bench-scale jar test experiments with model water). Conditions: a. and b. - pH 8, \( G=30 \text{ s}^{-1} \), \( t_f=30 \text{ min} \), and c., d., and e. - pH 8, 3 mg Fe(III)/L, \( t_f=10 \text{ min} \).
The polyelectrolyte coagulant aid dose of 0.5 mg Superfloc C-573/L had resulted in larger flocs with lower density $p=0.72$, while the dose of 1.0 mg Superfloc C-573/L had produced smaller and denser flocs of $p=0.91$ (see also Fig. 6.7). Similarly, an increase of the flocculation $G$ from 10 to 23 s$^{-1}$ (and 30 s$^{-1}$) had resulted in a decrease of the mean floc size and the consecutive increase of relative density $p$ from 0.86 to 0.91 and 0.93 respectively (Fig. 6.4). The results confirm an inverse dependence of relative density to floc size, as well as inverse dependence of floc size and flocculation $G$.

Calculations results for the jar tests with model water regarding the effect of ozone conditioning and different treatment combinations are presented in Fig. 6.17. As observed in this figure (compare data for raw water and ozonated water in Figs. 6.9 and 6.10) ozone induced microflocculation produced flocs of lower density ($p=0.81$) and larger size. This effect of ozone conditioning on the reduction of flocs relative density was even more pronounced than the one caused by the 3 mg Fe(III)/L coagulant dose ($p=0.91$). Higher reduction of floc density and increase of floc size was caused by the combination of ozone conditioning and iron coagulant ($p=0.74$, see also Fig. 6.10), while the inclusion of Superfloc C-573 in the ozone + Fe treatment scheme resulted in the opposite trend of producing denser and smaller flocs ($p=0.78$, see also Fig. 6.11). The last treatment scheme led to the highest DAF particle removal efficiency. Finally, the ozone + Superfloc C-573 coagulant combination resulted in floc density and size characteristics similar to the iron only case ($p=0.88$), however accompanied by comparably higher DAF efficiency (see also Section 4.3.3.c). This suggests that although the particle size-density ratio plays an important role in determining the DAF process efficiency, efficient particle destabilisation and surface charge related effects play a more determining role.

![Graph](image)

**Fig. 6.17** Relative floc density $p$ (eqs. 3 and 4) for different treatment combinations including ozone conditioning (0.2 mg O$_2$/mg TOC), and a reference situation with only Fe(III) treatment (bench-scale). Conditions: ozonation pH 7.5, coagulation pH 7.5±0.2, $G=10$ s$^{-1}$, $t_f=10$ min.

Calculation results for jar tests with model water regarding the effect of KMnO$_4$ conditioning are presented in Fig. 6.18. Similar to the case of ozone conditioning, the permanganate induced microflocculation resulted in larger and lower-density flocs ($p=0.89$ after 1 min contact time,
before coagulant addition, see also Fig. 6.13), while the effect of longer contact time was not so pronounced (p=0.85 for 30 min contact time before coagulant addition). The iron coagulant further reduced the floc density and increased the floc size, as observed after 10 minutes flocculation (p=0.74).

![Graph](image)

**Fig. 6.18** Relative floc density p (eqs. 3 and 4) in case of KMnO₄ conditioning (bench-scale), after different contact time. Conditions: pH 8, 5 mg Fe(III)/L, Gₜ=70 s⁻¹, tₐ=15 min.

### 6.3.9 Considerations for modelling

Sedimentation is generally regarded as a process which is favoured by low flocculation G resulting in larger flocs with supposedly good settling characteristics [35]. Our bench-scale analysis showed that better results were achieved at higher coagulant dose than applied in DAF (2-3 times higher) and resultant increase of the initial particle concentration after flocculation (Chapter 3). A flocculation G of 30 s⁻¹ resulted in smaller and denser flocs than at G=10 s⁻¹, with better settling characteristics [35]. Assuming constant water temperature and viscosity μ [ML⁻¹T⁻¹] and laminar flow conditions (Re<1), the sedimentation efficiency is proportional to settling velocity \( v_s [LT⁻¹] \) which is defined by the floc size \( d_f [L] \) and density \( ρ_f [ML⁻³] \):

\[
v_s = g \ d_f^2 \ ( ρ_f - ρ_w ) / 18 \ μ \tag{3}
\]

Attempts of modelling of DAF are primarily focussed on the reaction zone (region where the saturated recycle flow is introduced) or the separation zone. DAF modelling is discussed in more detail in Chapter 7. According to the single collector collision efficiency DAF model [10, 36], the efficiency in the reaction zone is expressed as d\( N_f / dt \) (reduction of number of primary particles - flocs with time), and depends on floc and bubble sizes (\( d_f [L] \) and \( d_b [L] \)), their concentration (\( N_f [L⁻²] \) and \( Φ_b [L^3/L^3] \)), the single collector collision efficiency coefficient \( η_T \), and the particle-bubble attachment efficiency \( α_{pb} \):

\[
dN_f / dt = - ( 3/2 ) \ ( α_{pb} \ η_T ) \ ( Φ_b \ v_b \ N_f ) / d_b \tag{4}
\]
Particle (floc)-bubble interception is considered the most relevant mechanism in DAF; it depends on the floc and bubble sizes \(d_f\) and \(d_b\) and is incorporated in the \(\eta_T\). This term also covers particle/floc-bubble collision by Brownian diffusion, settling and drag. Efficient particle removal by DAF generally requires smaller flocs than sedimentation, which should also be of preferably lower density [35]. Particles should be larger than 1 \(\mu\text{m}\), preferably of few tens of micrometers size, in combination with bubbles in the size range of 10-100 \(\mu\text{m}\) and a concentration that is one to two orders of magnitude higher [10, 36]. Our experiments showed that \(\alpha_m\) is significantly affected by surface charge, which also affects DAF via the floc concentration \(N_f\) and its size distribution \(d_f\) and \(\eta_f\), as in the case of coagulation pH 6 versus pH 7, 8 and 9 given in Figs. 6.3.a through 6.3.d, or when cationic polyelectrolyte was used as coagulant aid versus Fe coagulant treatment given in Figs. 6.6 and 6.7.

Assuming laminar flow conditions, the efficiency of the separation zone as expressed by the floc-bubble agglomerate rising velocity \(v_{fb}\) is defined by the floc-bubble agglomerate size \(d_{fb}\) and density \(\rho_{fb}\):

\[
v_{fb} = \frac{g \ d_{fb}^2 (\rho_w - \rho_{fb})}{18 \ \mu}
\]

Equation (5)

\[
v_{fb} > v_{os} / (1-m)
\]

Equation (6)

\(d_{fb}\) and \(\rho_{fb}\) depend on the floc size - density ratio and concentrations, and the size and number of bubbles comprising the floc-bubble agglomerate. Equation (6) describes a prerequisite for efficient DAF, with \(v_{os}\) the DAF overflow rate and \(m\) the fraction of DAF tank dead space [35].

In the case of DAF experiments with model water, similar particle removal efficiency was obtained both at the low \(G\) value of 10 \(\text{s}^{-1}\) (mean particle removal of 61.4\%) and that of \(G=70\ \text{s}^{-1}\) (mean particle removal of 61.7\%) although the resultant floc size - density ratios were different. Increase of the flocculation time further increase particle removal efficiency in case of the \(G\) value of 10 \(\text{s}^{-1}\) (mean particle removal of 67.2\%), while it decreased the removal efficiency for the \(G\) value of 70 \(\text{s}^{-1}\) (mean particle removal of 54.0\%). The equations for the reaction and separation zone suggest that DAF efficiency should be comparable in both cases (considering the measured mean floc size of \(d_f=15-20 \ \mu\text{m}\), and the mean bubble size of \(d_b=40 \ \mu\text{m}\)). The \(v_{fb}\) in both cases was approximately 3 \(\text{m/h}\), implying efficient floc removal in the available 4 minutes of flotation during the DAF jar tests. The larger and weaker flocs are susceptible to the shear effect of the recycled flow. Generally low flocculation \(G\) and resulting weak flocs are considered a drawback for efficient DAF, but this may be compensated by the production of flocs that are larger (thus causing higher \(\alpha_{fb}\) due to interception) and less denser (and thus easier to be lifted to the surface).

Although the relative density equation and the adopted coefficient values apply to monodisperse suspensions such as was the case with our model water, similar calculations were carried out for the heterodisperse reservoir water in the pilot plant experiments. At a coagulant dose of 10 \(\text{g Fe(III)/m}^3\) and 0.3 \(\text{g Superfloc C-573/m}^3\) best turbidity removal after DAF was obtained at \(G=50\ \text{s}^{-1}\) (89.9\%), typically 1-2\% higher than at \(G=10\) and 30 \(\text{s}^{-1}\) (Fig. 5.18). Image analysis data (Fig. 6.5) showed more efficient flocculation for this \(G\) value, expressed as highest reduction of the concentration of primary particles (thus lowest number of particles after flocculation \(N_f\)) and formation of larger size flocs with lowest density \(p=0.72\). In the case of tapered flocculation (Fig.
6.6) the second flocculation stage increased the volume of the larger particle size range while reducing the volume of smaller particles, and resulted in a decrease of relative floc density (from p=0.71 to 0.61). It is suggested that the relatively high coagulant doses (>10 g Fe(III)/m³) in combination with cationic polyelectrolyte coagulant aid resulted in a high $\alpha_{pb}$. In general, process efficiency tended to increase with increasing floc size (based on image analysis data mean floc size rose up to $d_f=40 \mu m$) and decreasing relative floc density (as low as p=0.61), this is in accordance with the DAF kinetic model.

Referring to eqs. (3) and (4) it is suggested that for a constant raw water quality (thus constant $\rho_w$ and $\mu$, as well as colloidal and particulate matter concentration and composition) and varied coagulation/flocculation conditions (coagulant dose, pH, flocculation G and flocculation time), it may be possible to define the settling efficiency expressed as $\nu_s$ (3), or the floc-bubble agglomerate rising velocity $\nu_{fb}$ (4) in the form of a surface area ($\nu_s$ or $\nu_{fb}$ on z-axis) in function of the resulting variations of floc or floc-bubble agglomerate size ($d_n$ or $d_{mb}$ on x-axis) and floc or floc-bubble agglomerate density ($\rho_n$ or $\rho_{mb}$ on y axis). This may possibly be achieved by the application of the statistical response surface methodology [33, 34]. This technology aims at overcoming the weaknesses of the classical one-variable-at-a-time strategy, such as e.g. assessing sedimentation or flotation efficiency (expressed as $\nu_s$ or $\nu_{fb}$) as a function of floc and floc-bubble agglomerate size ($d_n$ or $d_{mb}$) or density ($\rho_n$ or $\rho_{mb}$) separately. It consists of a group of techniques which can be used in empirical studies of relationships between one or more responses, such as in our case sedimentation or flotation efficiency (expressed as $\nu_s$ or $\nu_{fb}$), and a number of simultaneous input variables, such as in our case floc or floc-bubble agglomerate size ($d_n$ or $d_{mb}$) and density ($\rho_n$ or $\rho_{mb}$). This prospect seems achievable with the latest developments in computer image analysis technology.

6.4 CONCLUSIONS

Particle counting techniques (e.g., HIAC or similar) are being recognised as a parameter of filter effluent quality. This technique can be applied to a limited degree to sedimentation and DAF effluents, since the residual coagulant may significantly influence the count. An additional drawback may be the possible floc break-up due to high shear forces during the passage of the sample through the recording chamber, which discards it for characterisation of flocculated water. The computer image analysis technique, on the other hand, allows more qualitative and quantitative characterisation of the coagulation/flocculation process (with a size limitation of 1.9 $\mu m$). Characterisation of particles in the size range <1 $\mu m$ will substantially improve the qualitative and quantitative assessment of the coagulation/flocculation process.

To achieve efficient sedimentation it appeared necessary to increase the frequency of the larger particle size fraction (>50 $\mu m$), and to increase the overall particles concentration. This is generally achieved by higher coagulant doses than required for DAF. For efficient DAF on the other hand, increase of the larger particle size (>50 $\mu m$) on account of the disappearance of the smaller size fraction (<50 $\mu m$) was necessary. This was more pronounced at coagulation pH <1IEP (pH 6, compared to 7, 8 and 9), while at the same time, the smaller particle size fraction removal was improved by the achieved particle charge neutralisation. The latter phenomenon is related to the reduction of the particle - bubble repulsion (related to the negative charge of air bubbles) and resulting increase of the $\alpha_{pb}$. 
In the model water experiments low flocculation G= 10 s\(^{-1}\) contributed significantly to the larger particle size fraction which resulted in more efficient DAF, than at higher G values. On the other hand, low to medium flocculation energy input of G=10-30 s\(^{-1}\) resulted in more efficient sedimentation, the latter value resulting in a denser floc structure and higher sedimentation efficiency (relative floc density of p=0.93 versus 0.86).

Particle charge neutralisation achieved by cationic coagulant aid application raised the α\textsubscript{ab}, as well as the sedimentation efficiency; a 0.5 mg/L dose resulted in floc material favoured by DAF, and a 1.0 mg/L dose favoured by sedimentation. The cationic polyelectrolyte shifted the particle (floc) size distribution towards the higher size range; a higher polyelectrolyte dose resulted in denser floc structures (relative floc density of p=0.91 versus 0.72, for 1.0 and 0.5 mg Superfloc C-573/L).

Ozone and KMnO\(_4\) induced flocculation improvements that were mostly related to EOM and IOM release, resulting in spontaneous microfloculation and visibly affecting the particle size-density relationship before the addition of coagulant. A 0.2 mg O\(_3\)/mg TOC without the application of coagulant resulted in relative floc density p of 0.81, while the 0.7 mg KMnO\(_4\) dose resulted in a relative floc density of 0.89 after 1 min contact time, further decreasing to 0.85 after 30 min contact time. Different treatment combinations using ozone, iron and polyelectrolyte coagulant were tested. The production of flocs in the larger particle size range, created by ozone conditioning and iron coagulant (0.2 mg O\(_3\)/mg TOC + 3 mg Fe(III)/L), resulted in relative floc density of p=0.74 and in improved DAF efficiency, as compared to the case of 3 mg Fe(III)/L and the resultant p=0.91. Although inclusion of the Superfloc C-573 coagulant aid resulted in an opposite trend in terms of the relative floc density (p=0.78), the DAF process efficiency still increased suggesting that particle (algae) destabilisation and surface charge related effects determine it. The application of the polyelectrolyte Superfloc C-573 as a sole coagulant for ozone conditioned model water experiments demanded larger doses to achieve efficient particle destabilisation, which resulted in dense floc material (p=0.88) and relatively good DAF efficiency, mainly related to the efficient particle surface charge effects.

Bubble size distribution was affected by the recirculation flow conditions. Higher saturation pressure resulted in a slight decrease of the mean bubble size to theoretically more efficient sizes (from approximately 60 to approximately 50 μm), as well as in a narrower distribution. Higher recirculation ratios resulted in an increase of the bubbles concentration and of the distributions width. The overall high bubble concentration, and the generally high bubble concentration to particle concentration ratio is suggested to be an important factor determining DAF efficiency.

Reservoir water pilot plant experiments showed a comparable effect on the particle volume distribution in the larger size range for all tested G values (G=10, 30 and 50 s\(^{-1}\)), and similar particle removal efficiency. However, an increase of the G created better contact opportunities for the colloidal and particulate matter, reducing the number of smaller particles (<50 μm) and turbidity more pronouncedly (p=0.72). A lower velocity gradient in a second flocculation stage (G reduced from 50 to 30 s\(^{-1}\)) increased the volume of larger size particles at the expense of smaller ones and reduced the relative floc density from p=0.71 to 0.61.

The kinetics and particle removal efficiency for DAF and sedimentation were found to be defined by the particle agglomeration (coagulation/flocculation). The increase of the larger particle (floc)
size fraction resulted in a relative floc density decrease and a consecutive increase in DAF efficiency. While for sedimentation the floc size - density relation directly affects the efficiency, bubble size and bubble concentration are an additional factor of influence for DAF. Particle and bubble characterisation can further allow calculation of the floc size - density ratio (p) and the absolute floc density ($\rho_f$), important parameters in DAF and sedimentation model equations.

REFERENCES


Fig. 8.11 schematizes the possible scenarios related to the choice of DAF or sedimentation. It considers algae problems and other treatment related issues, including environmental and available space for treatment unit construction, as the core issues of concern. On the other hand, the wide range of raw water quality and process characteristics that affect process efficiency calls for pilot plant experiments as basis for cost-benefit analysis of possible treatment options. This should enable the enhancement of existing DAF or sedimentation facilities possibly by some of the options considered in this study. The same applies for the design of new and efficient (enhanced) DAF or sedimentation facilities, and even retrofit DAF when existing sedimentation cannot cope with high algae loads.

Knowledge and experience with the history of the raw water quality is essential for coping with current and future algae problems. Experienced DAF or sedimentation plant operators can cope efficiently with the algae concentrations occurring during the longest part of the year. Seasonal algae blooms will still pose a particular threat. Importantly, periodical outbreaks of certain new algal species or comparable organisms are possible, as was the case with the recent Cryptomonas spp. bloom in the WRK III reservoir. Timely algae monitoring is an essential tool for anticipating the problem at short notice.

8.9 CONCLUSIONS

-Coping with high algal loads (algal blooms) in water treatment with the philosophy that “the more algae are removed, the better” is not always the most feasible and cost effective approach to the problem. An efficient solution to the problem requires an approach which combines simultaneous, and continuous water quality monitoring, (reservoir) water quality management and application of latest developments in drinking water treatment technology.

-The total phosphates concentration which is to probably result in troublesome algal blooms (>10 μg chlorophyll-α/L) in surface water impoundments lies >0.05 mg/L. The predominant algal species, however, will depend on a range of additional factors, including the water pH, the combined ratio of other nutrients, water temperature, light availability, the presence of zooplankton grazers, etc.

-The cyanobacteria in general, and Microcystis aeruginosa and Oscillatoria agardhii in particular, are the most relevant species in Dutch water treatment circumstances, regarding the amount of related treatment problems.

-Dissolved air flotation (DAF) is a viable treatment alternative to conventional sedimentation for the removal of particulate matter and algae in particular. It is an efficient, robust, reliable and flexible, high rate treatment technology which is to be highly considered in case of treatment design for waters with expected long or short term algae related problems.

-The coagulation/flocculation process plays and essential role in determining the down-stream process efficiency, irrespective of, however, defined by the applied process (DAF, sedimentation or filtration).

-Otimal DAF algae removal (>2.75 μm) requires approximately 50% less coagulant than
sedimentation, with considerable accompanying cost savings and positive environmental implications. This, however, is accompanied with less efficient sweep coagulation conditions (partly due to complexing of the metal coagulant with the organic matter) than achieved by the high coagulant doses usually applied in the sedimentation, and results in higher residual turbidity, residual coagulant and modified fouling index (MFI) values.

-Highest DAF efficiency can be achieved at a coagulation pH below the iso-electrical point (IEP), related to the positive effect of adsorption coagulation occurring under these pH circumstances, which aids the predominantly occurring sweep coagulation (dosage dependant). Under normal drinking water treatment pH conditions (pH 7-8.5), the applicability of this option for process enhancement is generally not feasible on long term, however, its application during short periods of algae blooms is an attractive option worthy of consideration.

-Although DAF operated efficiently at a high flocculation G value of 70 s⁻¹ (which is generally related to the production of small, shear resistant flocs able to withstand the high shear from the introduction of the recycle flow), a low flocculation G value of 10 s⁻¹ resulted in similar or higher process efficiency (the lower shear resistance being compensated by the larger size and lighter floc structure obtained at lower G values).

-Increase of flocculation time for the lower G value resulted in further increase of DAF efficiency, which was not the case for the high G value. The emerging suggestion of the possible existence of an optimal Gt value range could not be verified.

-The optimal flocculation time for DAF is significantly shorter than for sedimentation (more than twice). Under normally encountered drinking water treatment pH conditions of 7-8.5, however, flocculation times shorter than 15 min are not recommended, in view of the insufficient downstream DAF efficiency (<90%).

-Tapered flocculation did not significantly affect DAF process efficiency. It is suggested that the total flocculation time plays a greater role in this respect than the tapering effect of diminishing energy input in consecutive flocculation stages.

-The application of cationic polyelectrolytes as coagulant aids significantly increased process efficiency in case of model water bench-scale experiments. This efficiency improvement is related to the promotion of adsorption coagulation. Efficiency improvements were absent in case of the non-ionic (Wisprofloc-N) and anionic (Superfloc A-100) polyelectrolytes, while efficiency differences also existed between the two cationic polyelectrolytes (Superfloc C-573 outperformed Wisprofloc-P). The latter is related to their charge and molecular weight characteristics.

-Similarly, the application of cationic polyelectrolytes as sole coagulant in DAF treatment proved efficient; Superfloc C-573 outperformed Wisprofloc-P. The application of cationic polyelectrolytes as sole coagulants is attractive due to the absence of metal coagulant residuals, however, the absence of a suitable residuals determination technique precludes their application, due to uncontrolled carcinogenic monomer residuals.

-The application of ozone as an algae conditioner can significantly raise DAF process efficiency at relatively low doses (0.2 mg O₃/mg TOC, or 0.5 mg O₃/L). This process enhancement option
is, however, restricted due to bromate formation. Its applicability is dependent on raw water quality (e.g. ozonation pH preferably <7) and stringency of applied drinking water regulations. If the EU guideline of 10 μg BrO₃⁻/L maximum allowable concentration (MAC) is considered, ozone algae conditioning may still be an attractive option.

- The application of KMnO₄ as an algae conditioner proved a potentially beneficial option for enhancing the algae coagulation/flocculation and subsequent removal by DAF, compounded by the absence of health hazardous by-products.

- Both, ozone and KMnO₄ resulted in significant modification of the algal cell wall structure, release of extra-cellular organic matter (EOM) and in-tra-cellular organic matter (IOM) leakage from lysed algal cells, and the promotion of spontaneous microflocculation, even before the coagulant was added.

- The application of cationic polyelectrolytes in the combined Fe(III) coagulant-ozone or KMnO₄ conditioning treatment scheme, can further increase DAF algae removal efficiency. Furthermore, it can reduce the residual iron (organio-iron complexes) and the colloidal MnO₂, below their MAC values.

- The flocculation process affects DAF or sedimentation efficiency via the resultant floc size - density relation. The relative floc density (in relation to the original density of particles incorporated in the floc) decreased with increasing floc size. The floc size increased as a consequence of decreasing pH, decreasing G values (as single stage or as part of the tapered flocculation concept), ozone or KMnO₄ conditioning (spontaneous microflocculation occurred) and cationic polyelectrolyte coagulant aid application. Increase of the polyelectrolyte coagulant aid dose, however, increased the relative floc density.

- Comparison of bench-scale experiments with model water and pilot plant experiments with reservoir water implicates that the efficiency of the coagulation/flocculation and down-stream process (DAF or sedimentation) is significantly influenced by the natural organic matter concentration and composition. The process efficiency recorded in the reservoir water experiments (high organic matter content, mostly humic matter) was significantly higher than the one recorded in the model water experiments (low organic matter content, already treated by ozone in full scale treatment).

- The high NOM content of the reservoir water asserted a high coagulant demand in order to meet the stringent MFI value of 5 s/L². For a given coagulant dose, the impact of the flocculation G value and the application of cationic polyelectrolyte coagulant aid were less significant for the DAF process efficiency compared to the model water circumstances. The flocculation time was of greater significance for process efficiency, while contrary to model water experiments no charge neutralisation occurred in case of the cationic polyelectrolyte application.

- The existence of NOM organic matter meshes and fibrilar structures is suggested partly responsible for the higher efficiency of the coagulation/flocculation process in case of the reservoir water experiments. The organic matter meshes also served as sites for floc and MnO₂ entrapment. Furthermore, they favoured efficient DAF, providing a gel-like structure which is efficiently removed by the rising air bubbles.
The solution of the particle removal efficiency equation of the single collector collision efficiency DAF kinetic model yielded $\alpha_{pb}=0.04-0.75$ for the jar test experiments and $\alpha_{pb}=0.26-1.0$ (1.79) for the pilot plant DAF experiments. The higher range of values were accomplished under optimal jar test coagulation/flocculation conditions ($\alpha_{pb}=0.39$), and in case of enhanced coagulation due to coagulation pH<IEP ($\alpha_{pb}=0.42$) or due to application of cationic polyelectrolyte as coagulant aid ($\alpha_{pb}=0.75$); for pilot plant conditions the application of coagulant doses of 10-15 g Fe(III)/m$^3$, alone or in combination with 0.5 g Superfloc C-573/m$^3$ resulted in high $\alpha_{pb}=0.26-1.0$ values.

High DAF particle removal efficiencies (>90%) are related to the accomplishment of high particle-bubble attachment efficiency ($\alpha_{pb}$ values >0.5).

The model showed higher sensitivity of the $\alpha_{pb}$ for particle floc size than bubble size. Modification of the bubble size distribution by variation of the recirculation ratio and saturator pressure has little impact on process efficiency, suggesting that high recirculation ratios (>7%) and saturator pressures (>500 kPa) are not always justified.

The single collector collision efficiency DAF kinetic model can be a valuable tool in the design of DAF facilities and experimental design. However, the role of water quality factors which affect the coagulation/flocculation process and DAF, such as NOM concentration and composition, must also be considered. In this context, the basic assumption of the model that particle-bubble agglomeration occurs solely due to their collision is not fully justified.
WK IN RESERVOIR WATER
- turbidity > 5 (10) FTU
- particle (algal) count of size ≥ 2.75 μm
  after microstraining N = 10-20 × 10^3/mL
- chlorophyll-a
  (01.09.95-15.11.95) = 28.8 μg/L
  (01.09.96-15.11.96) = 29.3 μg/L

### MICROSTRAINING & INITIAL STAGE PUMPING

<table>
<thead>
<tr>
<th>BENEFICIAL PROCESSES</th>
<th>POTENTIAL RISKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ straining - removal of zooplankton</td>
<td>■ fast blocking of the mesh pores by filamentous and colonial algal species (e.g., O. agardhii and M. aeruginosa)</td>
</tr>
<tr>
<td>■ straining - removal of large, filamentous and colonial species (e.g., O. agardhii and M. aeruginosa), resulting in more frequent washing and servicing during algal blooms</td>
<td>■ reaction with functional groups on algal surface → no risk for increased Fe residual before filter</td>
</tr>
<tr>
<td>■ break-up of alga colonies (e.g., of M. aeruginosa) into difficult to remove single cells</td>
<td>■ initial spontaneous algae flocculation</td>
</tr>
<tr>
<td>■ growth of and interference by CaCO₃ crystals</td>
<td>■ continuing reactions of NOM with ozonides, organic peroxides, and organic free radicals, after O₃ has disappeared</td>
</tr>
</tbody>
</table>

### OZONE CONDITIONING

<table>
<thead>
<tr>
<th>BENEFICIAL PROCESSES</th>
<th>POTENTIAL RISKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ disinfection</td>
<td>■ bromate formation</td>
</tr>
<tr>
<td>■ DOC (and AOC) oxidation and improved removal in subsequent flocculation stage of smaller aromatic compounds</td>
<td>■ break-up of colonial alga species (e.g., M. aeruginosa) into difficult to remove single cells</td>
</tr>
<tr>
<td>■ break-up of organo metal complexes, in-situ coagulant production</td>
<td>■ cell lysis and IOM leakage</td>
</tr>
<tr>
<td>■ reaction with organic matter on particle surface and reduced particle stability</td>
<td>■ rise of AOC</td>
</tr>
<tr>
<td>■ increased sorption of ozonated NOM on hydrolysed metal hydroxide flocs,</td>
<td>■ rise of taste and odour problems if taste and odour causing algae are present</td>
</tr>
<tr>
<td>■ increased Ca complexation with NOM</td>
<td>■ rise of (cyanobacteria related) toxicity</td>
</tr>
<tr>
<td>■ improved taste and odour</td>
<td>■ rise of (Fe-NOM complexation)</td>
</tr>
<tr>
<td>■ improved GAC operation and adsorption of organic matter, including pesticides</td>
<td>■ possible negative effect on polymer structure (break-up of polymer chains)</td>
</tr>
<tr>
<td>■ possibly reduced coagulant demand (Fe), depending on organic matter structure and reaction mechanism with ozone (conflicting literature data)</td>
<td>■ possible need for pH correction before ozone application (rapid decomposition, as well as increased bromate formation at pH&lt;7.5)</td>
</tr>
<tr>
<td>■ zooplankton and plankton conditioner</td>
<td>■ zooplankton and plankton conditioner</td>
</tr>
<tr>
<td>■ immobilisation of motile algae and organisms, easier floc entrapment</td>
<td>- immobilisation of motile algae and organisms, easier floc entrapment</td>
</tr>
<tr>
<td>■ reaction with functional groups on algal surface → no risk for increased Fe residual before filter</td>
<td>- reaction with functional groups on algal surface → no risk for increased Fe residual before filter</td>
</tr>
<tr>
<td>■ reduction of algal surface charge</td>
<td>- excretion of EOM and IOM → production of biopolyelectrolyte coagulant aids</td>
</tr>
<tr>
<td>■ excretion of EOM and IOM → production of biopolyelectrolyte coagulant aids</td>
<td>- initial spontaneous algae flocculation</td>
</tr>
<tr>
<td>■ initial spontaneous algae flocculation</td>
<td>- continuing reactions of NOM with ozonides, organic peroxides, and organic free radicals, after O₃ has disappeared</td>
</tr>
</tbody>
</table>

### KMnO₄ CONDITIONING

<table>
<thead>
<tr>
<th>BENEFICIAL PROCESSES</th>
<th>POTENTIAL RISKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ (mild) disinfection power at common water treatment doses (max = 3-4 g/m³)</td>
<td>■ increased residual Mn values (MnO₂ and dissolved Mn)</td>
</tr>
<tr>
<td>■ DOC (and AOC) oxidation</td>
<td>■ increased residual Mn</td>
</tr>
<tr>
<td>■ adsorption of oxidised DOC onto MnO₄⁻ precipitate</td>
<td>■ increased AFO before filter</td>
</tr>
<tr>
<td>■ break-up of organic-metal complexes → in-situ coagulant production</td>
<td>- pink colour (dissolved Mn)</td>
</tr>
<tr>
<td>■ accelerated flocculation through MnO₄⁻ precipitation → increased particle concentration</td>
<td>■ break-up of colonial alga species (e.g., M. aeruginosa) into difficult to remove single cells</td>
</tr>
<tr>
<td>■ improved taste and odour</td>
<td>■ cell lysis and IOM leakage</td>
</tr>
<tr>
<td>■ reduction of THM formation potential</td>
<td>- rise of AOC</td>
</tr>
<tr>
<td>■ zooplankton and plankton conditioner</td>
<td>- possible rise of taste and odour problems (depending on KMnO₄ dose and taste and odour compounds</td>
</tr>
<tr>
<td></td>
<td>- reaction products)</td>
</tr>
<tr>
<td>■ immobilisation of motile algae and organisms, easier floc entrapment</td>
<td>- rise of (cyanobacteria related) toxicity</td>
</tr>
<tr>
<td>■ excretion of EOM and IOM → production of biopolyelectrolyte coagulant aids</td>
<td>- possible rise of THM (conflicting results in literature)</td>
</tr>
<tr>
<td>■ initial spontaneous algae flocculation</td>
<td>- possible rise of THM (conflicting results in literature)</td>
</tr>
</tbody>
</table>
Table 8.2  Schematized process mechanisms, including beneficial processes and potential risks occurring during (enhanced) DAF treatment of algae laden water.
Samenvatting


De mate van eutrofiëring van het ruwe water dat door de drinkwaterbedrijven wordt gezuiverd, is aan sterke schommelingen onderhevig. Fosfor is hierbij de limitierde nutrient gebleken. Concentraties van meer dan 0.05 mg P/L zijn potenti al problematisch in de zin van algengroei (>10 µg/L). De predominant algenpopulaties zijn afhankelijk van een scala van aanvulende factoren zoals pH, temperatuur, de verhouding met andere nutrienten, licht intensiteit, etc. Als gevolg van de fluctuaties in algenpopulaties (van gemiddeld 8.4 µg/L chlorophyll-a voor het Loenderveense Plas tot gemiddeld 238 µg/L chlorophyll-a voor het PWN-bekken) treden zuiveringsproblemen op. Uit veld-onderzoek bleek dat cyanobacteriën in het algemeen, maar vooral Microcystis aeruginosa en Oscillatoria agardhii soorten, de hardnekkigste soorten zijn en de meeste zuiveringsproblemen gaven. De Nederlandse ervaringen zijn over het algemeen representatief voor geindustrialiseerde landen waar eutrofiëring gewoonlijk resulteert in een opbloei en hieraan gekoppeld in zuiveringsproblemen. Deze problemen bestonden uit een tot 100% verhoogde vlokmiddelbehoefte, substantieel verhoogde hoeveelheden filterspoelwater, trihalomethaanvorming (gedurende korte perioden van onderbrekingen in chloorering voor controle van mosselgroei), (oppervlakte) verstopping van filters, het door algen passeren van de behandelingsinstallatie in bezwaarlijke hoeveelheden, een verhoging van de MFI (Membrane Fouling Index) en de AOC (Assimilable Organic Carbon) waarden, enz. De ook voorkomende eencellige M. aeruginosa is qua grootte (3-10 µm) en geaardheid representatief voor de pathogene Cryptosporidium oocysten en de Giardia cysten, die in de behandeling zijn bijzonder moeilijk te verwijderen.

Deze studie richtte zich op de verwijdering van de cyanobacterie M. aeruginosa door conventionele en meer geavanceerde behandelingsmethoden, die beschikbaar zijn of die als haalbaar beschouwd worden voor de kwaliteit van ruw water en de procesomstandigheden in Nederland. Zuiveringsmethoden die in de betrokken bedrijven toegepast worden omvatten sedimentatie-filtratie en de meer geavanceerde DAF (Dissolved Air Flotation)-filtratie. Het coagulatie/floculatie-proces is van doorslaggevend betekenis voor de efficiëntie van voornoemde zuiveringstrappen, onafhankelijk van het zuiveringssysteem. De mogelijkheid van algenconditionering door oxidatiemiddelen zoals ozon of KMnO₄, werd als aantrekkelijk beschouwd om (tijdelijk of continu) de efficiëntie van de algenverwijdering te vergroten, alhoewel deze methode in Nederland niet toegepast wordt. Daarom richtte deze studie zich op een onderzoek naar een reeks zuiveringsmogelijkheden voor de verwijdering van M. aeruginosa, met de nadruk op DAF. Naast de efficiëntie van het proces werd aandacht besteed aan de procesmechanismen.
In deze studie worden twee experimentele opstellingen gebruikt: te weten een op laboratorium schaal ontwikkeld voor zowel DAF als sedimentatie, en een semi-technische DAF proefopstelling (Purac, Zweden). Voor de eerste opstelling werd modelwater gebruikt dat bereid was uit water afkomstig uit de Biesbosch reservoirs waaraan een laboratoriumculture van *M. aeruginosa* (beginconcentratie van ≈ 10.000 cellen/mL) was toegevoegd. De standaardtemperatuur van de experimenten was 20°C en de coagulatie snelheidsgradient G was 1.000 s⁻¹ voor een duur van 30 s bij een pH 8. Andere coagulatie-omstandigheden werden ook getest (pH 4, 6, 7, 8 en 9). De flocculatie G en de tijd werden gevarieerd (G = 10, 30, 50, 70, 100 en 120 s⁻¹ en tₖ = 5, 10, 15, 25, 30 en 35 min.). De vlokmiddel doses waren 0 - 15 mg Fe(III)/L, terwijl de kationische polyelectrolieten Superfloc C-573 en Wisprofloc-P, het non-ionische Wisprofloc-N, en het anionische Superfloc A-100 zijn getest als enige vlokhulpmiddelen. Ozon werd gebruikt als een algen-conditioneer in de dosierbereik van 0.48-2.16 mg O₃/L of 0.2-0.9 mg O₃/mg TOC bij een pH 7.5. KMnO₄ behandeling werd getest in het dosierbereik van 0-2 mg/L bij een pH 8 waarbij de optimale dosis werd afgeleid met behulp van een visuele determinatie techniek. De KMnO₄- contacttijd werd gevarieerd tussen 0 en 30 min. Na de DAF behandeling (capaciteit installatie 4-6 m³/h) werd het water over een op-waars bedreven drielagensnelzandfilter gevoerd (v=10 m/h). Beide behandelingen zijn gesitueerd in de WRK III zuiveringsinstallatie in Andijk, Nederland. Het resultaat werd vergeleken met het zuiveringsrendement van WRK III zuiveringsssysteem dat bestaat uit flocculatie, lamellenbezinking en - zandfiltratie. Analysetechnieken om doelmatigheid van het proces in te schatten bestonden uit bepaling van troebelheid, het restzijdegehalte, TOC/DOC, UV absorptie bij 254 nm en het restmangaangehalte. Bovendien werden meer geavanceerde methoden toegepast bestaande uit bromaat en MFI-metingen, telling van deeltjes (in het afmetingenbereik van d>2.75 µm, en in een beperkt aantal gevallen d>0.3 µm) en computer beeldanalyse. Deze laatste methode biedt, gekoppeld met een hoge resolutie SEM (Scanning Electron Microscopy), waardevolle informatie om de proces mechanismen te schatten.

Voor de behandeling van algenrijk water (o.m. *M. aeruginosa*) is DAF een doelmatig alternatief voor sedimentatie gebleken. Zo resulteerde DAF behandeling in een gelijk of beter rendement van algenverwijdering dan het sedimentatieproces (71% vergeleken met 87% voor bekerproef-testomstandigheden en 96.3% vergelijken met 95.6% voor de proefinstallatie omstandigheden), terwijl zij tegelijkertijd een 50% lagere vlokmiddeldosis vereisten dan de sedimentatie (3 mg Fe(III)/L vergeleken met 10 mg Fe(III)/L in de laboratoriuminstallatie en 7-12 g Fe(III)/m³ vergeleken met 20-24 g Fe(III)/m³ + 0.2-0.5 g Wisprofloc-P/m³ in de proefinstallatie). Bovendien had het geproduceerde slib een hoger droge stofgehalte. Andere gunstige aspecten waren onder andere de relatief korte flocculatietijd (echter, niet korter dan 15 min, vergeleken met >30 min voor sedimentatie) en de lage hoeveelheid energie nodig voor de flocculatie (G = 10 s⁻¹ vergeleken met G = 30 s⁻¹ voor sedimentatie), zowel als de hoge belasting van het proces (over het geheel leidend tot 5-6 keer minder procesruimte). Bovendien, het DAF-filtratie behandelingsschema resulteerde consequent in een hoge (>2 log) efficiëntie in algenverwijdering. Echter, de relatieve kleine vlokhulpmiddeloefte voor DAF zorgde voor minder efficiënte omstandigheden dan bij sedimentatie, wat resulteerde in vorming van organo-Fe complexen en dientengevolge hogere ijzergehalten en reststroeling van het slotaat. Dit werd opgelost door toepassing van kationische vlokhulpmiddelen, of door instelling van een pH die lager ligt dan de pH van het IEP (Iso-Electrical Point). De verbetering in het rendement van de deeltjesverwijdering (algen) was duidelijkder bij de experimenten met modelwater (20-40%, en
maar 1-2% in experimenten met de proefinstallatie). Dit is te wijten aan de bevordering van adsorptie coagulatie van deeltjes (algen) wanneer de lading geneutraliseerd is. Bovendien, de geobserveerde verschijnselen van neutralisatie van de lading resulteerden in een verbeterde hechting tussen deeltjes-bei en dus een efficiëntere DAF. Non-ionische en anionische polyelectrolyten werden minder efficiënt bevonden, gedeeltelijk vanwege de lage deeltjesconcentratie (lagere vlokmiddeldosis) en de negatieve lading op de lichtbellen.

Het rendement van de algenverwijdering met de proefinstallatie ligt 20-30 % hoger dan de bekerproeven met modelwater. Waarschijnlijk was de NOM (Natural Organic Matter) concentratie en samenstelling de oorzaak van deze verschillen, vooral omdat het aanwezig is in de vorm van netwerken van organisch materiaal en in de vorm van draadvormige structuren. Hoewel het complexeren van de metaal vlokmiddelen door NOM een extra vlokmiddelbehoeft geeft, zullen deze structuren uiteindelijk coagulatie bevorderen, omdat zij kunnen dienen als plaatsen voor vlokgroei en hechting en ook een gel-achtige structuur bieden zodat deze gemakkelijker is te verwijderen door de flotatie.

Op laboratorium-schaal bleken relatief lage doses ozon (0.2-0.5 mg O₃/mg TOC of 0.6-1.5 mg O₃/L) gebruikt als algenconditioner de DAF efficiëntie significant (40-50%) te verhogen (2 log verwijdering). Gecombineerd met kationische polyelectrolyten werd de DAF efficiëntie nog 5 % beter. De toepassing van de lagere dosis van 0.2 mg O₃/mg C bij pH 7 resulteerde in bromaat niveau’s onder de 10 µg/L MAC (Maximum Allowable Concentration), zoals voorgeschreven door de EU, alhoewel dit resultaat nog niet bevestigd is in de praktijk op semi-technische schaal. De voortgaande verbetering van de verwijdering van organische stof door aktief-koolfiltratie zou het belang van deze behandeling vergroten, speciaal als de ozon al gebruikt wordt voor andere doeleinden binnen de zuivering (bijv. desinfectie) en alleen als de MAC-waarde onder de huidige voorgeschreven concentratie blijft.

Het gebruik van KMnO₄ als een algen conditioner leidde ook tot een verhoging van de DAF-proces efficiëntie, hetgeen resulteerde in een gelijkwaardig of beter rendement dan in het geval van de conventionele sedimentatie technische schaal, in enkele gevallen zelfs in een betere prestatie dan in het geval van technische schaal sedimentatie + filtratie wat betreft de deeltjesverwijdering (d > 2.75 µm). Echter, als gevolg daarvan was de restijzer concentratie (organo-Fe-complexen) en Mn (over het algemeen MnO₂) hoger, wat het aantal deeltjes van colloïdale afmeting (<0.5 µm) en de troebelheid deed toenemen. Deze situatie verbeterde toen de kationische polymeer geïntroduceerd werden als vlokhulpmiddelen, wat significant de efficiëntie van het DAF proces verbeterde (over het algemeen met 5%) door reductie in Fe en Mn-concentraties onder hun respectievelijke MAC-waarden. Maar deze mogelijkheid verlaagde niet de concentratie van het begeleidende filtraat MFI tot de gewenste waarde van 5 s/L². De laagste MFI-waarde die bereikt werd door de niet geoptimaliseerde filtratie (binnen het DAF + filtratie schema) was ongeveer 20 s/L². Dit suggereert de behoefte aan optimaliseren van de filtratiestap om geheel de conditionerende werking van KMnO₄ te gebruiken.

De verbeterde algenverwijdering in het geval van het conditioneren door een oxidatiemiddel is waarschijnlijk veroorzaakt door een aantal processen. Beweeglijke algencellen worden geïmmobiliseerd door oxidatie van delen van de buitenste cellaag, waardoor hun stofwisselingsprocessen verstoord worden. Dit gaat gepaard met struktuurwijzigingen in de algen, resulterend in EOM (Extra-cellular Organic Matter) uitscheiding, gedeeltelijke algen ontbinding.

Verschillen in de verkregen deeltjesgrootteverdelingen en deeltjesvolumeverdelingen vormden de basis voor een discussie over de invloed van procesomstandigheden. Deze verdelingen maakten ook een profondervindelijke berekening mogelijk van de relatieve en absolute vlokdictheid, die een input-variabele is in het beschouwde DAF-model. Andere input-variabelen zoals de gemiddelde deeltjes (vlok) en belgrootte, alsook aantallen en volume-concentraties van deeltjes en bellen werden tegelijkertijd gemeten of berekend. De berekende waarden voor de hechtinsefficiëntie van deeltje aan luchtbel, αₚₑ, ondersteunen de geponeerde stellen betreffende de positieve invloed van kationische vlokhulpmiddelen en conditioners. De resultaten suggereren dat onder optimale flotatie omstandigheden bijna de helft van de bostingen tussen deeltjes (vlokken) en bellen resulteert in hechting. De recirculatie verhouding (5-10%) en de verzadigingsdruk (500-700 kPa) bleken minder essentieel te zijn voor de proces-efficiëntie, alhoewel zij de belgrootte aanzienlijk beïnvloeden. Derhalve eist het coagulatie/flocculatie-proces als de meest bepalende factor van het DAF-proces alle aandacht. Alhoewel moeilijk te modelleren is de invloed van de NOM-concentratie en karakteristieken op de hechtinsefficiëntie van deeltje en luchtbel van groot belang. Op deze manier is een vereenvoudigde model benadering dat deeltjesluchtballen opeenlopig allen het resultaat van hun botsing is, niet geheel gerechtvaardigd.

DAF blijkt een efficiënt, robuust en flexibel proces en is zeer geschikt als alternatief voor sedimentatie bij de zuivering van met algen belast water. De lagere investeringskosten en het lagere chemicaliën verbruik zullen vaak de hogere energie- en onderhoudskosten compenseren. De efficiëntie inzake algenverwijdering maakt deze vorm van flotatie aantrekkelijk als voorbehandeling voor directe filtratie of membraanfiltratie. Waar het al wordt toegepast kan de efficiëntie tijdelijk vergroot worden (met name gedurende algenbloei) door toepassing van met name kationische vlokhulpmiddelen, oxidatiemiddelen, of een combinatie van beiden. De toepassing van KMnO₄ lijkt bijzonder aantrekkelijk, omdat geen enkele bezwaarlijke bijproducten ontstaan. De uiteindelijke keuze van de behandelingstechnologie dient eventueel na een onderzoek met een proefinstallatie en een kosten-baten analyse gemaakt worden.
Curriculum Vitae

Aleksandar Vlaški was born in Skopje, Macedonia on November 14, 1958. After attending primary school and gymnasium in Skopje, he received a B.Sc. degree in civil engineering in 1984 from the University of Cyril and Metodij in Skopje.

In 1984 he started his professional career as an assistant design engineer in the hydro-department of the “EMO-Institute for Energetics” in Skopje, a scientific and consulting daughter institution of the largest electronics company in Macedonia EMO-Ohrid. In 1987 he joined the Sanitary engineering department, where he formally stayed until 1992, advancing to a position of independent design engineer, with full responsibility for the design of different sanitary engineering projects. He was involved on a number of national and international projects of various nature: hydro-power plants and energetics, regional and rural water supply and distributions, regional and rural wastewater collection, and drinking water, wastewater and industrial wastewater treatment. He performed a variety of engineering tasks, including hydraulic and process technology design, site engineering, project management and finally project acquisition.

In 1989 he came to the Netherlands to the International Institute for Infrastructural, Hydraulic and Environmental Engineering (IHE), Delft, where he obtained a post-graduate diploma in sanitary engineering in 1990. In 1991 he returned to IHE and conducted his M.Sc. research on a joined project between IHE and the Technical University (TU), Delft, dealing with ‘Aggregation of algae and direct filtration’. After seven months he concluded his research by obtaining his M.Sc. Degree with distinction in Environmental Engineering from IHE Delft.

From January 1993 until October 1997 he worked on what started as a joint research project between the IHE and TU Delft titled ‘Relevance and removal of cyanobacteria in water treatment’. After two years of work at the Civil Engineering Faculty, Laboratory for Sanitary Engineering, and two and a half years of work at the IHE Delft, he concluded the research with a Ph.D. thesis titled ‘Microcystis aeruginosa removal by dissolved air flotation (DAF) - options for enhanced process operation and kinetic modelling’.

In November 1997 he joined the engineering and consulting company Tauw Milieu, Deventer, at the position of a drinking water treatment process technologist.
The aim of the International Institute for Infrastructure, Hydraulic and Environmental Engineering, IHE Delft, is the development and transfer of scientific knowledge and technological know-how in the fields of transport, water and the environment.

Therefore, IHE organizes regular 12 and 18 month postgraduate courses which lead to a Masters Degree. IHE also has a PhD-programme based on research, which can be executed partly in the home country. Moreover, IHE organizes short tailor-made and regular non-degree courses in The Netherlands as well as abroad, and takes part in projects in various countries to develop local educational training and research facilities.

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