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COAGULATION AND FLOCCULATION OF DISSOLVED ORGANIC SUBSTANCES WITH ORGANIC POLYMERS

By

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In memory of my father
Audun Kvinnesland
(1934-1997)

ABSTRACT

Coagulation of natural organic matter (NOM) in water is a well-established process, enabling or enhancing the removal of these substances by different particle separation processes. The dominating coagulating agents used are, however, inorganic salts of iron (Fe^{3+}) and aluminium (Al^{3+}). The primary use of organic polymers is as flocculating agents for already coagulated aggregates. However, in recent years the use of cationic organic polymers have received increasing attention as coagulating agents, used alone or in combination with the traditional metal salt coagulants.

The objective of this study was to determine how organic cationic polymers can coagulate dissolved organic substances in water. The main focus has been on how differences in chemical composition and charge density of the polyelectrolytes affect their efficiency as coagulants. This was achieved by comparing the efficiencies of low molecular weight poly-Epi-amine, polydiallyldimethylammonium chloride, cationic polyacrylamide and chitosan in jar test experiments on constructed humic water as well as on wastewater biofilm reactor effluent. In order to compare the coagulation of dissolved organic substances as such with the following flocculation of aggregates, sequential filtration through filters of decreasing pore diameters (11 µm through 0,1 µm) was chosen as the particle separation method.

All polyelectrolytes tested were efficient in coagulating NOM in humic water and reached approximately the same maximum levels of coagulation, however, different dosages were required for the different polyelectrolytes.

Results from experiments on humic water at pH 6 indicated that the differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain. Furthermore it was shown that the effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such. Experiments performed at pH 4 indicated that the effect of charge addition that was dominating at pH 6 is less pronounced at pH 4.

Using sequential filtration as the particle separation method showed that the coagulation of dissolved organic substances in particle free humic water by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima. With respect to the relationship between coagulation of dissolved organic matter and flocculation in the experiments on biofilm reactor effluent, significant differences in performance were observed with chitosan relative to the synthetic polyelectrolytes. In general, the results indicated that chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate matter, than the synthetic polyelectrolytes tested.

Direct comparisons of results obtained on particle free humic water and particle rich biofilm reactor effluent indicated strong similarities in the dosage response with respect to coagulation of dissolved organic substances. The presence of particles and adsorption of polyelectrolyte to these did not appear to negatively affect the coagulation of dissolved organic matter with polyelectrolyte. Rather, there appeared to be a positive effect of the presence of particulate matter on the polymer dose efficiency in coagulation of dissolved organic matter.

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SUMMARY

Coagulation of natural organic matter (NOM), of which humic substances traditionally have received the main focus, is a well established process, enabling or enhancing the removal of these substances by particle separation processes such as settling, filtration, dissolved air flotation, and recently also membrane filtration. The dominating coagulating agents used are however inorganic salts of iron (Fe^{3+}) and aluminium (Al^{3+}). The primary use of organic polymers is as flocculating agents for already coagulated aggregates. However, in recent years the use of cationic organic polymers have received increasing attention as coagulating agents, used alone or in combination with the traditional metal salt coagulants.

The objective of this work has been to determine how organic cationic polymers can coagulate dissolved organic substances in water. The main focus has been on how differences in chemical composition and charge density of the polyelectrolytes affect their efficiency as coagulants. A set of hypotheses (A through G) was formulated on basis of the findings from the literature study.

The selection of polymer types consisted of polydiallyldimethylammonium chloride (PDADMAC), poly-Epi-amine, cationic polyacrylamide and chitosan. The main objective in choice of polymers for testing was to directly compare the efficiency of a broad range of low molecular weight, cationic polyelectrolytes. It was also of special interest to compare the weakly charged biopolymer chitosan with different synthetic, strongly charged polycations, and furthermore to investigate the effect of the degree of acetylation of chitosans on their efficiency as coagulants for dissolved organic matter. A medium molecular weight cationic polyacrylamide was included in order to investigate the effect of molecular weight on coagulation of dissolved organic matter.

Most of the experiments were performed as jar tests. In order to compare the coagulation of dissolved organic substances as such with the following flocculation of aggregates, sequential filtration through filters of decreasing pore diameters was chosen as the particle separation method.

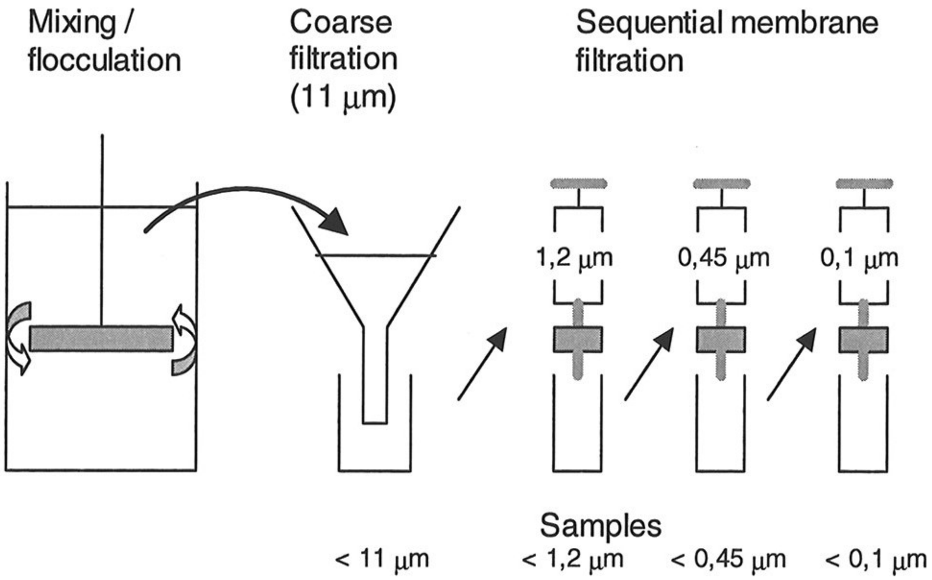


Figure I. Physical set-up of main experiments (schematically)

The experiments were performed on two very different raw water types: a constructed, particle free humic water and a particle rich wastewater biofilm reactor effluent. In most of the experiments the pH of the raw waters were adjusted to pH 6 prior to addition of polyelectrolyte coagulants. However, an additional set of experiments were performed on humic water at pH 4 to investigate the effect of pH on coagulation of NOM with a strong (PDADMAC) and a weak (chitosan) polycation. The main intention in the choice of different raw water types was to investigate the interaction of cationic polyelectrolytes with different kinds of dissolved organic substances and under different conditions.

Dissolved substances have in this study been defined operationally as substances passing a 0,1 μm membrane filter. Coagulation has accordingly been defined as the formation of aggregates that are withheld in a 0,1 μm membrane filter. Quantitatively, coagulation has been defined and measured as the removal of dissolved organic matter from the raw water:

Coagulated matter = Dissolved matter in raw water sample
- Dissolved matter in sample of coagulated water

The results from the experiments on humic water using sequential filtration as the particle separation method showed, in support of hypothesis A, that coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima. The polyelectrolyte dosage providing maximal coagulation of dissolved organic substances lies substantially higher than the dosage providing aggregates with the best flocculation properties.

With respect to the relationship between coagulation of dissolved organic matter and flocculation in the experiments on biofilm reactor effluent, significant differences in performance were observed with chitosan relative to the synthetic polyelectrolytes. With the synthetic polyelectrolytes the results indicated that acceptable flocculation of particles and new-formed aggregates first takes place after all coagulable dissolved organic matter has been coagulated. Chitosan appeared to be more capable of acting both as coagulant and flocculant than the synthetic polyelectrolytes at low dosages.

In general, the results indicated that chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate matter, than the other polyelectrolytes tested.

All polyelectrolytes tested were efficient in coagulating NOM in humic water and reached approximately the same maximum levels of coagulation, however different dosages were required for the different polyelectrolytes. Colour removals after filtration through 0,1 μm up to 95% were observed for all polyelectrolytes. TOC removals were lower reaching a maximum of 45-50%. In the experiments on biofilm reactor effluent removals of COD after filtration through 0,1 μm up to 35 % were observed.

Results from experiments on humic water at pH 6 indicated, in support of hypothesis B, that differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain. Furthermore, in support of hypothesis C, it was shown that the effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such.

Experiments performed at pH 4 indicated that the effect of charge addition that was dominating at pH 6 is less pronounced at pH 4. It was suggested that that there may exist alternative mechanisms for the interactions between NOM and cationic polyelectrolytes (probably related to interaction between non-polar segments of NOM and polyelectrolyte), and that the relative importance of these depend on pH and the charge density of the NOM.

The experiments with PDADMAC on humic water at pH 4 demonstrated, in support of hypothesis E-1, increased coagulation of NOM with a given dosage of polyelectrolyte relative to coagulation at pH 6. The results with chitosan at pH 4 indicated a less pronounced effect of pH on coagulation dose efficiency than with PDADMAC and were therefore not in support of hypothesis E-2 (which predicted a stronger effect of pH on coagulation with a weak polycation than with a strong polycation).

Experiments on humic water comparing chitosans with different degrees of acetylation demonstrated that the chitosan with the lowest degree of acetylation ($F_A = 0,05$), and therefore the highest cationic charge density, exhibited higher polymer dose efficiency with respect to coagulation of humic substances than the more highly acetylated chitosan ($F_A = 0,37$). Furthermore it was shown that, again in support of the hypotheses (B and C) on the importance and nature of the effect of polyelectrolyte charge density, the difference in dose efficiency was predominantly an effect of the addition of different amounts of charge equivalents when dosing equal amounts of the two chitosans, and not an effect of the differences in relative fractions of acetylated and deacetylated glucoseamine groups in the chitosans.

The results on low molecular weight cationic polyacrylamide (CPAAM) compared to those of medium molecular weight CPAAM gave, in support of hypothesis D, no indications of a positive effect of increased molecular weight on coagulation of NOM in humic water.

Results from experiments combining the use of iron chloride sulphate and cationic polyelectrolytes (PDADMAC and chitosan) indicated, in support of hypothesis F, that the polyelectrolyte dose necessary to facilitate a given degree of coagulation of dissolved organic substances in humic water, as well as in biofilm reactor effluent, could be significantly reduced when combined with a low dosage of a metal salt coagulant. In both systems a strong dependence on pH was observed.

Direct comparisons of results obtained on particle free humic water and two different batches of particle rich biofilm reactor effluent indicated strong similarities in the dosage response with respect to coagulation of dissolved humic-like (UV-absorbing) substances as well as dissolved TOC by cationic polyelectrolytes. The presence of particles and adsorption of polyelectrolyte to these did not appear to negatively affect, by competing for the polyelectrolyte molecules, the coagulation of dissolved organic matter with polyelectrolyte. Rather, there appeared to be a positive effect of the presence of particulate matter on the polymer dose efficiency in coagulation of dissolved organic matter.

LIST OF SYMBOLS AND ABBREVIATIONS

AA	Acrylamide
AA-DMAEA	Copolymer of acrylamide and dimethyl aminoethyl acrylate
BDOC	Biodegradable organic carbon
COD	Chemical oxygen demand
F_A	Degree of acetylation (in chitosans)
CD	Charge density
CPAAM	Cationic polyacrylamide (copolymer)
CPMA	Cationic polymethacrylate
DOC	Dissolved organic carbon
Epi	Epichlorohydrin
EPM	Electrophoretic mobility
HMW	High molecular weight
HS	Humic substances
ICP-MS	Inductively coupled plasma - mass spectrometer
LMW	Low molecular weight
MBBR	Moving bed biofilm reactor
MMW	Medium molecular weight
MW	Molecular weight
NOM	Natural organic matter
NPOC	Nonpurgeable organic carbon
NTU	Nephelometric turbidity units
PDADMAC	Polydiallyldimethylammonium chloride
PEI	Polyethyleneimine
R_G	Radius of gyration
SUVA	Specific UVA (UVA per mg organic carbon)
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
UV	Ultraviolet (light)
UVA	UV (ultraviolet) absorbency
VHA	Very hydrophobic acids (ascribed to humic acids)

Decimal point notation

Notice that the comma (,), not the point (.), has been used as the decimal point notation.

TABLE OF CONTENTS

1 INTRODUCTION

It can easily, and understandably, be stated that the title of this thesis (*Coagulation and flocculation of dissolved organic substances with organic polymers*) contains a contradiction in terms. Dissolved substances don't coagulate, they precipitate or adsorb. Particles that are suspended, not dissolved in a thermodynamic understanding, and stabilized with respect to flocculation coagulate. So why call it coagulation of dissolved substances? The main motivation of this thesis, investigating the interaction between dissolved organic substances and cationic organic polymers, is to contribute to a greater understanding on how cationic organic polymers function in the removal of humic substances from water. In this context coagulation appears to be the established term in the water treatment community. In the same community the established definition of dissolved substances is operational, not thermo dynamical, related to whether the substances pass filters of a certain, usually sub micron, pore diameter. By this definition the majority of the organic substances we seek to *coagulate* are in fact *dissolved.* As it has not been an ambition in this work to actually prove whether the organic substances are truly thermodynamically dissolved or whether they actually precipitate rather than coagulate as result of the interaction with organic polyelectrolytes, the choice of terms has been coagulation of dissolved substances.

Coagulation of natural organic matter (NOM), of which humic substances traditionally have received the main focus, is a well established process, enabling or enhancing the removal of these substances by particle separation processes such as settling, filtration, dissolved air flotation, and recently also membrane filtration. The dominating coagulating agents used are however inorganic salts of iron (Fe^{3+}) and aluminium (Al^{3+}). The primary use of organic polymers is as flocculating agents for already coagulated aggregates. However in recent years the use of cationic organic polymers have received increasing attention as coagulating agents, used alone or in combination with the traditional metal salt coagulants.

The advantages of using organic cationic polyelectrolytes instead of, or as supplement to, the traditional metal salt agents in coagulation of natural organic matter are several. One of the most important is that the organic polymers do not react with, and alter the chemical properties of, the water itself to the same extent as metal salt coagulants. They do not alter pH and alkalinity of the water, add substantially less to the total ion content of the water, nor do they form large amounts of inorganic precipitates, which is the case with metal salt coagulants. Thus, sludge formation is substantially lower and with a lower water content with cationic polyelectrolyte coagulants than with metal salts, allowing for longer filter run times in depth filtration processes and lower sludge handling costs in general. Whereas the efficiency of metal salts coagulants is strongly dependent on water pH, the relative pH-independence of most cationic organic polyelectrolytes (weak polycations such as chitosan being the exception) in their interaction with natural organic matter is often considered to be an important advantage.

The major disadvantages with organic cationic polymers as coagulants are related to the presence, or possibility of, product residuals in the water. There are serious health concerns related to the use of many synthetic cationic polyelectrolytes, mainly due to the possibility of residual monomers in synthetic polymer products. But also residuals of the polymers themselves are unwanted, as they constitute substrate for bacterial growth as well as the formation of disinfection by-products. Till now the occurrence of residual polymer in treated waters have received sparse attention and is poorly understood. Regrettably this work does not contribute to a greater understanding of this problem, but it is natural to assume that the monitoring of polymer residuals will have to be given more attention in studies on the use of organic polymer coagulants and flocculants.

This work has been accomplished in an institute with long traditions and experience in the study of coagulation and flocculation, with inorganic as well as organic coagulants. Nevertheless, with respect to polymers the same questions appear to resurface: What will be the best polymer in a given situation and why? These questions constitute the main motivation and objective of this study.

2 THEORY – LITERATURE STUDY

2.1 Scope and focus of the literature study

The main objective of this work has been to study the interaction between dissolved organic substances and cationic organic polymers, in general and with cationic polyelectrolytes of different chemical composition. This main objective is also reflected in the literature study presented in this chapter. The main effort has gone into the study of literature specifically addressing dissolved organic substances and their interactions with different cationic polyelectrolyte coagulants. Most of the previous research concerning interactions, coagulation or precipitation, of dissolved organic substances with polymer coagulants has been focused on the removal of humic substances drinking water systems, that is coagulation of organic matter in natural waters. The emphasis of this chapter is therefore on characteristics and polyelectrolyte coagulation of humic substances.

Coagulation and flocculation with polyelectrolytes in general, and especially of particles, is a vast and well-studied field of science. No attempt has been made to present an extensive review on all sides of this subject. Again the emphasis has been placed on coagulation of dissolved organic substances, but a brief summary of some the main general issues concerning polyelectrolyte coagulation of particles is presented in the following sub-chapter.

One sub-chapter has been assigned to give a brief presentation of the cationic polymer coagulants used in this study as well a condensed introduction to important aspects relating to the shape (conformation) and physical size of polymers in solution.

2.2 Introduction to coagulation in water and wastewater treatment

Good representations on the general theory concerning the stability of impurities in water are offered in most basic textbooks on water chemistry, water- and wastewater treatment and colloidal chemistry and will not be repeated here. Instead this sub-chapter has been limited to offer a brief presentation of colloidal suspensions with organic polymers. Mechanisms involved in the coagulation of dissolved organic substances are treated separately in chapter 2.6.2.

There is no single mechanism of destabilization of colloidal suspensions by polymers that may account for all situations. However two principally different mechanisms are generally accepted to be the dominant.

Coagulation with low molecular weight, high charge density polyelectrolytes is by most investigators explained by the adsorption of an oppositely charged polyelectrolyte to the colloidal surface and thereby reducing the thickness of the electrical double layer surrounding the particles. The often-quoted electrostatic patch mechanism is a special case of this mechanism.

Coagulation (and flocculation) with high molecular weight, low charge density (or non-ionic) polymers is in most cases explained by the adsorption of different segments of one polymer molecule to different colloids and thereby linking them together in a bridge-like fashion, the so called bridging mechanism.

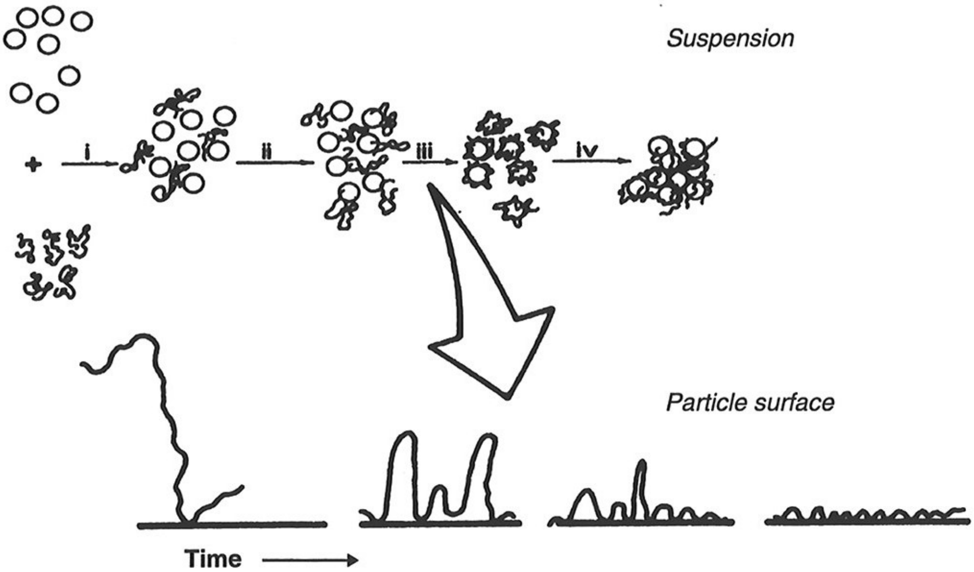


Figure 2.1. Stages in the adsorption of polymers on particle surfaces and destabilisation according to the bridging mechanism (from Bratby, 1980).

The bridging mechanism, schematically visualised in figure 2.1, can be divided into four stages (Bratby, 1980) as follows:

1. Dispersion of the polymer in the suspension
2. Adsorption of a polymer segment on the colloid surface
3. Compression of the adsorbed polyelectrolyte onto the colloid surface
4. Collisions between and attachment to adjacent polymer coated colloids

The main characteristic of the bridging mechanism is the aspect of time, or more precisely that it is restricted to occur before the adsorption of polymer molecules to the particle surface has reached equilibrium. After the polymer molecules have been dispersed and have diffused to the liquid-solid interface of the particles, adsorption is believed to occur initially with one segment or functional group. The rest of the polymer chain is momentarily dangling into the solution, (figure 2.1, ii). Adsorption can be due to ionic bonding, cationic exchange, electrostatic linkages or hydrogen bonding (Bratby, 1980). Subsequently Brownian motions will lead to adsorption at successively more points along the chain until the colloid-polymer configuration reaches a point where there are no more polymer ends but instead a number of pendant loops extending some distance into the solution (figure 2.1, iii). Progressively more points along the polymer chain will be attached to the colloid surface. Consequently the number and extension of the loops is reduced until the chain is compressed against the surface (figure 2.1, iv). The process from the initial adsorption of a few polymer segments, through the loops-formation, to full compression is reached requires a finite time. The efficiency of coagulation through bridging therefore depends on the collision frequency of the particles in the suspension relative to the time span during which the polymers assume a flat configuration on the particle surface. The bridging mechanism is also principally distinguishable by, and actually proposed as a result of, the fact that it may explain coagulation of charged particles with non-charged polymers.

Unlike the bridging mechanism, destabilisation or coagulation by means of charge neutralisation can occur after the polymer has reached equilibrium conformation on the particle surface on which it is adsorbed. As is evident from the name, coagulation according to this mechanism is caused by the reduction of the thickness of the electrical double layer due to the adsorption of oppositely charged polymers thereby enabling particle collisions to result in aggregate formation. The electrostatic patch mechanism proposed by Gregory (1973) can be considered as a special case of charge neutralisation and can be observed when the charge density of the polyelectrolyte is markedly higher than the surface charge density of the particles. This results in a charge mosaic pattern on the particle surface with alternating regions of initial particle surface charge density and regions where the net surface charge has been reversed due to the adsorption of oppositely charged polyelectrolytes.

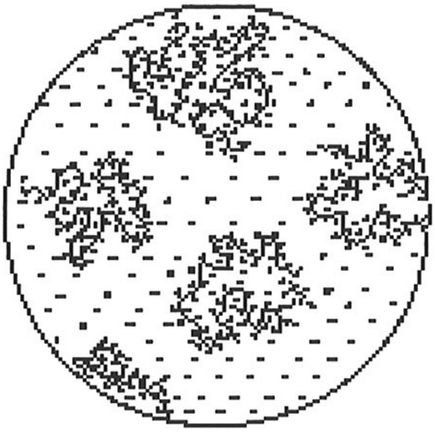


Figure 2.2. Possible arrangement of adsorbed polycations on negatively charged particle (Bratby, 1980).

The strong electrostatic attraction between aligned regions of opposite charge on adjacent particles causes the observed rates of aggregate formation to actually supersede the rates expected for diffusion limited coagulation.

2.3 Organic matter in natural waters

Natural organic matter (NOM) in water is generally divided into humic substances and non-humic material. The humic fraction of NOM has historically been considered as the most important from a water treatment point of view (Owen *et al*, 1995 referring to Thurman, 1985). The division into these two classes of compounds is to a great extent operational, based on differences in colour, hydrophobicity and complexity. Humic substances are generally hydrophobic, ill-defined complex macromolecules and constitute the main source of the yellowish-brownish colour in many natural waters (Jones and Bryan, 1998; Owen *et al*, 1995). In acidic solution and in the presence of metal ions humic substances exhibit properties characteristic of colloidal particles (Jones and Bryan, 1998). Non-humic materials generally are less hydrophobic, more easily defined and colourless molecules such as proteins, polysaccharides, nucleic acids and small molecules such as sugars and amino acids (Jones and Bryan, 1998; Owen *et al*, 1995).

Humic substances as well as non-humic substances found in natural waters are reactive with respect to chlorine and act as substrates in the formation of disinfection by-products (trihalomethanes and other halogenated hydrocarbons) (Breemen *et al*, 1979 referring to Dowty *et al*, 1975, Kissinger and Fritz, 1976, Rook, 1974). The reactivity with respect to THM formation of the non-humic fraction is comparable to that of the humic fraction. (Owen *et al*, 1995)

The non-humic fraction of NOM may contribute to a relatively greater part of the biodegradable organic carbon (BDOC) that serves as substrate for bacterial growth in water distribution systems than humic substances (Owen *et al*, 1995).

2.3.1 Humic substances

Humic substances are products of microbial decay of plant and animal residues in humification processes occurring in soil, sediments and water (Jones and Bryan, 1998 referring to Stevenson, 1982). They make up 60-70 % of soil organic matter and 30-50% of NOM in surface waters (Jones and Bryan, 1998 referring to Thurman and Malcolm, 1981, Woodwell *et al*, 1978). Considering the long time humic substances have been exposed to biodegradation, water, oxygen and radiation (sunlight) in the environment, they can be regarded as "old molecules", at the end of their biodegradative and oxidative route and unlikely to undergo further decomposition unless exposed to "new" chemical agents (Jones and Bryan, 1998).

Humic substances exhibit colloidal properties interacting with metal ions as well as human made pollutants and biocides, thereby affecting the mobility of these in the environment (Jones and Bryan, 1998). Acting as colloidal adsorbents, the presence of humic substances increases the total solubility of toxic heavy metals such as lead, copper and zinc as well as pesticides and halogenated hydrocarbons (Breemen *et al*, 1979 referring to Khan, 1972 and 1974, Poirrier *et al*, 1972, Wershaw *et al*, 1969, Choi and Chen, 1976). Humic substances also adsorb to other colloidals (mostly clay) found in natural waters and thus enhancing their colloidal stability (Jones and Bryan, 1998).

The chemical composition and structure of humic substances have received attention in research over many decades, but are presently still ill defined. In broad terms the structure of humic substances could be regarded as assemblies of covalently linked aromatic and aliphatic structures carrying functional groups such as carboxyl, phenolic and alkoxy (Jones and Bryan, 1998). Deprotonation of carboxylate groups and phenol groups give rise to the anionic charge observed for humic substances in solution (Jones and Bryan, 1998 referring to Livens, 1991). Numerous tentative structures have been proposed (Jones and Bryan, 1998), of which one is given in figure 2.3 below(adapted from Schulten and Schnitzer, 1993).

The three dimensional structure of humic molecules is believed to be significantly more compact than predicted by random modelling from their atom content, suggesting an overall contraction of the structure possibly related to their hydrophobic nature (Jones and Bryan, 1998). The molecular mass distribution of humic substances span from thousands to tens of thousand and higher (Jones and Bryan, 1998).

Humic substances are operationally divided into fulvic acids (soluble in water. at all pH-values), humic acids (soluble at pH > 2) and humins (insoluble at all pHs) (Jones and Bryan, 1998). Fulvic acids generally have a higher content of acidic functional groups (carboxylic and phenolic), and thus a higher anionic charge density, than humic acids. They have therefore been suggested to be more difficult to coagulate by charge neutralization (Owen *et al*, 1995). Fulvic acids are generally more hydrophilic than humic acids (Breemen *et al*, 1979 referring to Odèn, 1919). The relative proportions of humin and humic and fulvic acids found in natural waters are site-specific and constitute in sum approximately 35-70 % of total organic carbon, TOC (Thorsen, 1999).

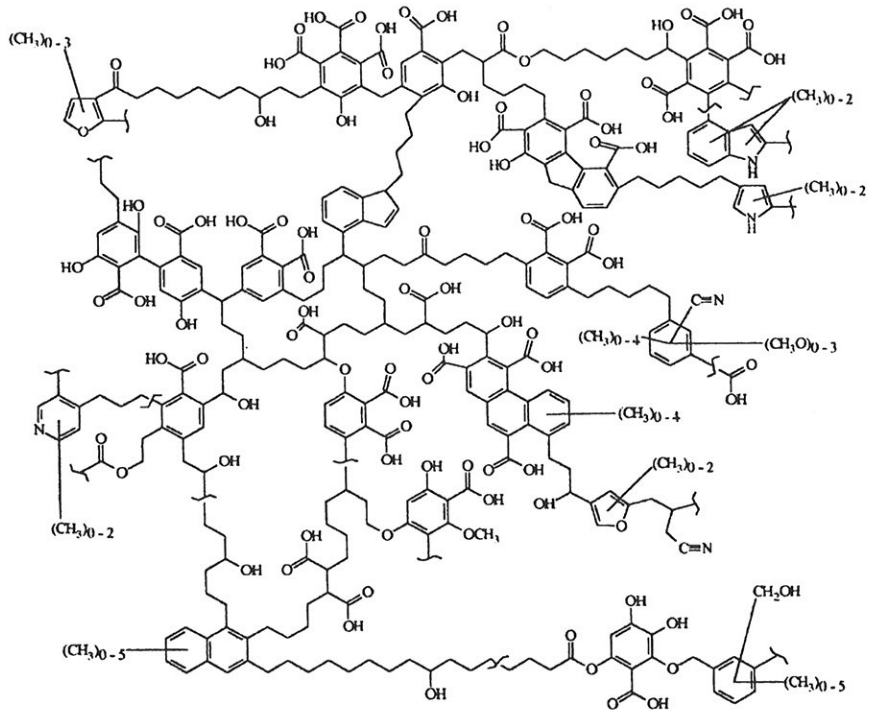


Figure 2.3. Structural concept of a humic acid proposed by Jones and Bryan (1998) as adapted from Schulten and Schnitzer (1993).

The content of ionisable functional groups such as carboxyl influences the solubility of humic substances (Owen *et al*, 1995, referring to Perdue, 1985) as well as their charge density. The pK_a of humic carboxyl groups have values between 4 and 6 (Stumm and Morgan, 1996) rendering humic substances negatively charged at pH values found in most natural waters. As with other charged macromolecules electrostatic repulsion between equal charges, stretching out the main chain, has a profound effect on the molecules size in solution (Thorsen, 1999).

The concentrations of humic substances in natural waters are usually measured indirectly as colligative properties such as light absorbency in the visible (colour) and ultraviolet (UV) wavelength range. Both visible light and UV absorbencies are sensitive to the presence of particles as well as solution pH, increasing pH resulting in increased absorbencies. Total organic carbon, TOC, is another frequently used measure of organic substances in water, including non-humic as well as humic NOM.

Contents of functional groups are frequently measured indirectly as carboxylic and phenolic acidities by potentiometric titration (Owen *et al*, 1995 referring to Perdue, 1985; Collins *et al*, 1986). Narkis and Rebhun (1977) found potentiometric titration curves of humic and fulvic acids to show two inflection points corresponding to the phenolic -OH groups (at pH 8,0 for humic and 8,2 for fulvic acids) and the carboxylic groups (at pH 4,9 for humic and pH 4,6 for fulvic acids).

With respect to determination of molecular weight distributions most available methods, including colligative properties, gel permeation chromatography, ultra filtration, ultra centrifugation, static and dynamic light scattering, viscometry, electron microscopy and more unconventional techniques such as field fractionation, have been applied to humic substances (Jones and Bryan, 1998, referring to Wershaw and Aiken, 1985), but no technique has proved itself as superior. Two major problems related to molecular mass determinations of humic substances are the great breadth of the mass distributions and the concentration-dependent tendency of humic molecules to aggregate.

Recently it has become more widespread to characterize NOM with respect to its relative proportions of fractions with different hydrophobicity and –philicity. Using a sequence of non-ionic, cationic and anionic resins (Bolto *et al*, 1998) NOM can be fractionated into four fractions with varying hydrophobicity:

- A very hydrophobic fraction (adsorbed by a XAD-8 non-ionic resin) ascribed to humic acids
- A weakly hydrophobic fraction (adsorbed by a XAD-4 non-ionic resin) ascribed to fulvic acids
- A hydrophilic negatively charged fraction (adsorbed by a anion exchange resin) ascribed to proteins, amino acids and anionic polysaccharides
- A neutral hydrophilic fraction (passing through all resins) ascribed to carbohydrates, aldehydes, ketones and alcohols

In two water sources (Bell Bay and Hope Valley), tested by Bolto *et al* (1998), humic acids made up around 45 % of the total TOC in the original waters, fulvic acids 15-20%, proteins (hydrophilic anionic fraction) around 30% and sugars (neutral hydrophilic fraction) up to 5%. Using a similar fractionation technique Levine *et al* (1996) found that the hydrophobic fraction of the total NOM of two water sources varied from 30 to 75%, depending heavily on seasonal changes.

Various investigators have observed some useful correlations between different measuring techniques and characteristical properties of humic substances. Ratnaweera *et al* (1999) demonstrated in an investigation including molecular weight dependent fractionation by ultra filtration of eight Norwegian water sources colour (visible light absorption), UV-absorbency and DOC content to be strongly inter-correlated regardless of water source and size-fraction. Levine *et al* (1996) found UV-absorption to be a specific measure of the content of aromatic groups and/or double bonds in the NOM. Breemen *et al* (1979) found coagulation with metal salts to preferentially remove the fulvic acid fraction with a relatively high carboxylic group content. The same fraction was responsible for 96% of the original colour, indicating correlation between the contents of carboxylic groups and chromophores. UV to TOC ratios, commonly referred to as SUVA or specific UVA, have for many different natural waters (Edzwald *et al*, 1985; Vik, 1982; Rook *et al*, 1982) been found to lie in the range of 4-5, and to depend on a waters relative content of humic substances, a significantly lower ratio indicating a higher relative content of non-humic organic matter. Colour and UV-absorbance (UVA), with the latter favoured, have by many investigators (Bolto *et al*, 1998, referring to Korshin *et al*, 1996, Frimmel and Hesse, 1996) been found to constitute good indicators of a waters trihalomethane formation potential (THMFP).

2.4 Polymer coagulants

The main objective of this subchapter is to give a brief presentation of the different polymer types used in this study. In addition a coarse introduction to the conformation and physical size of polymers in solution is offered. The latter is included because the shape and size a polymer chain takes in solution is easily, and often, misinterpreted, at least in the water treatment community.

2.4.1 Description of polymer types tested in this work

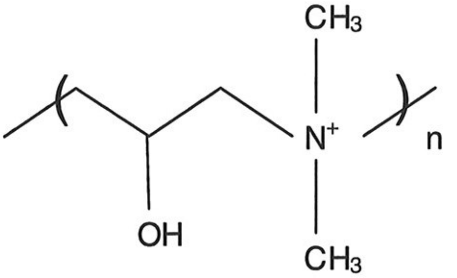
2.4.1.1 Classification of molecular weights

In the descriptions of the various polyelectrolytes used in this study the following classification of molecular weights has been adapted from Bolto (1995):

Low molecular weight (LMW)	$10^4 - 10^5$ Dalton
Medium molecular weight (MMW)	$10^5 - 10^6$ Dalton
High molecular weight (HMW)	ca. 10^7 Dalton

2.4.1.2 Poly-Epi-amine

Poly-Epi-amine is produced in the reaction of epichlorohydrin with a secondary amine such as dimethylamine (Bolto, 1995).



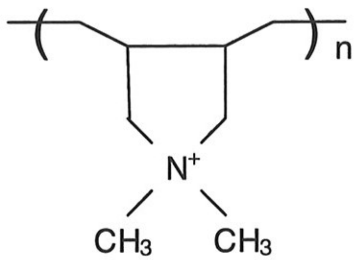
Poly-Epi-amine

Figure 2.4. Repeating unit of poly-Epi-amine. Note that the counterion has been omitted from the structure.

It is a linear, low MW homopolymer in which all the nitrogens are on the quaternary ammonium form and located within the main chain. It has the highest stoichiometric charge density (7,0 meq/g) of the polymers tested in this study.

2.4.1.3 PolyDADMAC

Polydiallyldimethylammonium chloride, commonly referred to as polyDADMAC (PDADMAC) is produced from the polymerisation of diallyldimethylammonium chloride. As with poly-Epi-amine all the nitrogens are in the quaternary ammonium form, but in PDADMAC they are located in the five-membered ring (pyrrolidinium unit) produced in the polymerisation reaction. It is a low to medium MW homopolymer with a stoichiometric charge density of 6,2 meq/g.



PDADMAC

Figure 2.5. Repeating unit of polydiallyldimethylammonium chloride (PDADMAC). Note that the counterion has been omitted from the structur.

2.4.1.4 Chitosan

Chitosan is a biopolymer produced from chitin, the water-insoluble structure polymer of the outer skeleton of insects and crustaceans. It is a low to medium MW heteropolymer consisting of uncharged N-acetylglucoseamine and weakly (pH-dependent) charged glucoseamine, obtained from a full or partial deacetylation of the N-acetylglucoseamine-groups of chitin. Different definitions exist with respect to the division between chitin and chitosan, but the following, proposed by Roberts (1992), appears to be particularly useful in a water treatment context: *Chitin and chitosan can be distinguished by insolubility (chitin) and solubility (chitosan) in dilute aqueous solutions.* Commercial products of chitosan normally contain 5 to 20 % acetylated units, distributed randomly along the chain. At pH-values above ca. 7 the amino groups are unprotonated rendering the molecule insoluble (the pK_a value of the amino group in chitosan is ca. 6,6 (Smidsrød and Moe, 1995)). Dissolution of chitosan is therefore conducted in an acidic environment.

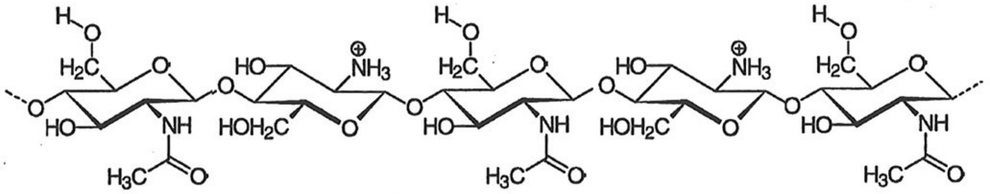


Figure 2.6. Section of the structure of chitosan (from Smidsrød and Moe, 1995). Note that the counterion has been omitted from the structure.

The stoichiometric charge density of chitosans is a function of the degree of acetylation F_A ($F_A = 1 -$ fraction of glucoseamine) and pH. The charge density decreases with increasing F_A and increases with decreasing pH. For a given F_A and pH it can be calculated according to formulas presented in appendix A.

It has not been possible to find reports on the influence of F_A on the efficiency of chitosans as a coagulant for dissolved organic substances. However, Strand (2001) recently tested chitosans of different F_A as coagulants (or flocculants) for bacteria and found their efficiency in flocculating *E. coli* to increase proportionally with F_A.

Being virtually non-toxic chitosan has a special potential as a primary coagulant in potable water treatment. The disadvantage of chitosan is that the commercially available products due to production costs are presently priced at a level unable to compete economically with synthetic cationic polymers or metal salts.

2.4.1.5 Cationic polyacrylamide (CPAAM)

Cationic polyacrylamides are a heterogenic group of polymers obtained from modifications of polyacrylamide (uncharged) or co polymerisations of quaternized dimethylaminoethyl acrylate or methacrylate. The exact composition and structure of commercial products are generally kept secret by the manufacturers, but the structure shown below is an example believed to be quite representative of the cationic polyacrylamides (CPAAM) used in this study.

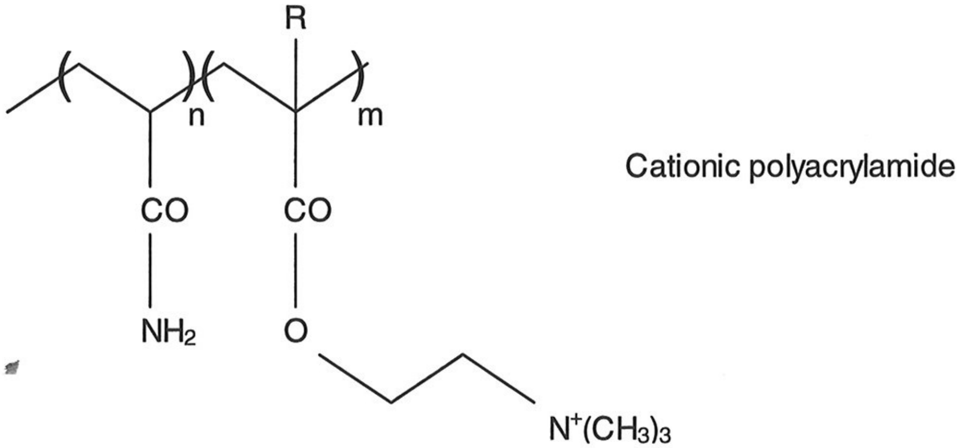


Figure 2.7. Example of normal repeating units of cationic polyacrylamide. Note that the counterion has been omitted from the structure.

Cationic polyacrylamides can be produced with molecular weights ranging from low to high and cationic contents ranging from 10 to 100 mol %. It should be noticed that copolymers of acrylamide may lose their cationic group in a hydrolysis of the ester groups taking place under alkaline conditions, roughly above pH 6 (Bolto, 1995):

$$\text{Pol-COOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 + \text{OH}^- \rightarrow \text{Pol-COO}^- + \text{HOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$$

The hydrolysis has been found to be dependent (increasing) on charge density and pH (Bolto, 1995). Solutions of the polymers should therefore be prepared at relatively low pH (around pH 4).

2.4.1.6 Counter ion condensation

It should be noted that the electrical field surrounding highly charged polyelectrolytes, such as those used in this study, could become so strong that some of the counter ions are trapped within very short distances of the polyion. Manning, who called the effect *counter ion condensation*, developed a theory predicting that there must be a minimum linear spacing, the *Bjerrum length*, between charges on a polyion. For water containing univalent counter ions the Bjerrum length calculates to 0,714 nm (25°C), but the Manning-theory is an approximation and, in practice, the Bjerrum length appears to be closer to 1 nm (Smidsrød and Moe, 1995). A highly charged polyelectrolyte has in other words a maximum effective linear charge density per Bjerrum length even though the stoichiometric charge density is higher. This means that the polymers in this study (polyDADMAC, quaternary polyamine, high charge density polyacrylamides and low F_A chitosans) have effective charge densities in solution that are significantly lower than the calculated stoichiometric charge density.

It is unclear whether this has practical consequences regarding their ability to neutralize opposite charges when adsorbing to an oppositely charged surface. Intuitively one would expect this effect to be cancelled out by the mutual neutralisation of charges at the surface and lowering of the electrical field surrounding the polyelectrolyte so that the stoichiometric charge density can be used to estimate the polymers charge neutralizing capacity at an oppositely charged surface.

2.4.2 The conformation of polymers in solution

As mentioned in the introduction to this subchapter on polymer coagulants, the motivation for including this brief introduction on polymer shape and size in solution is that these properties appear to be quite widely misunderstood and misinterpreted among researchers in the field of water treatment. This thesis itself regrettably does not draw lines between polymer conformation and their efficiencies as a coagulants and flocculants. However, the conformation of polymer chains in solution has a great influence on their physical properties as well as their technological applicability and so its plausible to assume that a rough understanding on this subject should be an advantage also in the field of water treatment. This brief presentation is to a large extent based on two very good books by Smidsrød and Moe (1995) and Grosberg and Khokhlov (1997) respectively. The presentation given below is intended to provide a rough, qualitative understanding of the most important aspects of polymer conformation from a water treatment perspective and offers by no means a complete, or just, account of the complexity and magnitude of this field of science.

Polymer chains in solution are often conceptionalised as stretched, rod-like strings and attempts to estimate the physical size of the molecules have been presented based on this conception. Appearing as linear structures in formulas, this visualisation of polymer chains is quite understandable, but it is not true. Very few, if any, of the polymers used in water treatment appear as stretched-out strings in solution, neither are they static structures. Polymer chains in solution are in most cases very flexible, dynamic structures constantly altering physical shape and extension. Thus describing their conformation and size it is important to realize that these are averages of the different shapes and sizes the molecules fluctuate between.

It is generally accepted that the average conformation of a polymer in a solution can be viewed as an approximation to, or more often a transitional shape somewhere between, three distinctly different idealized shapes: the compact sphere, the flexible coil and the stiff rod. The late professor Arne Haug at NTNU contributed with a visual presentation to simplify the understanding of the conformations of a polymer in solution. He put the three idealized conformations, the sphere, the rod and the flexible coil at the corners of a triangle (Smidsrød and Moe, 1995).

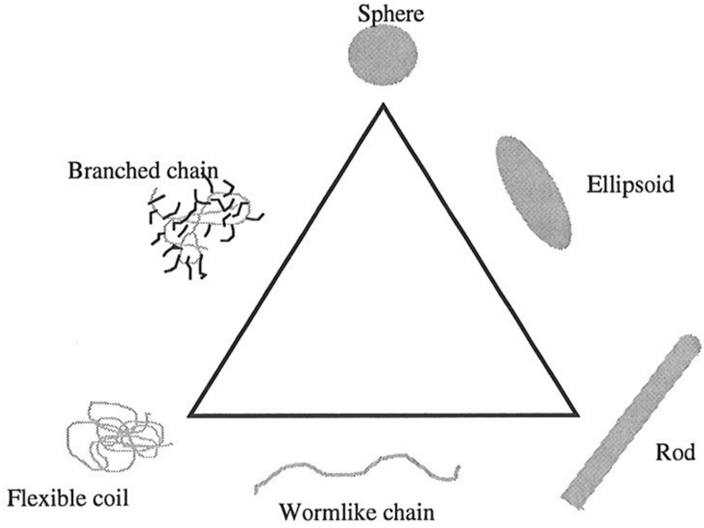


Figure 2.8. Haugs triangle. Possible conformations of a polymer in solution (from Smidsrød and Moe, 1995).

The conformation of a polymer in solution is a result of the structure and properties of the polymer itself and the properties of the solvent relatively to the polymer. In the theoretical efforts to explain and predict macromolecular conformations one usually starts out defining the molecules as statistical chains of vectors. The monomers are regarded to occupy no volume and there no are restrictions regarding bond-angles or steric obstructions. In this case the bonds in the chain can be viewed as vectors with directions that are under no influence of the directions of the other vectors. This leads to a very dynamic fluctuating structure called a freely jointed chain and represents a statistical-mechanical problem called random walk (similar to that of Brownian motions and diffusion). This idealized conformation is called a random coil or flexible coil. It is fluctuating around an average shape that is spherical. To approach the probable conformation of a more "realistic" molecule the theoretical model-development stepwise introduces restrictions regarding bond angles, rotation around the bonds and the actual excluded volume of the monomers.

Regarding only the polymer, the conformation in solution will mainly be determined by the basic geometry of the polymer chain itself, degree of rotational freedom of the bonds, steric obstruction and secondary (non-covalent) bonds and interactions between different segments of the chain (ionic forces, van der Waal forces). All of the polymers used in this study have conformations in solution lying on the axis between a flexible coil and a rod, but substantially closer to that of the flexible coil than that of the wormlike chain. There are, within the group of polymers tested, substantial differences in chain stiffness influencing the expansion and stretching of the coils. For example, the glycoside bond between the units of chitosan have substantially lower freedom with respects to bond angles and rotation than the methyl-methyl bonds of the other polycations, rendering chitosan a stiffer, more expanded molecule. A recently published report by Trzcinski *et al* (2002) demonstrates this very clearly for chitosan and PDADMAC.

When describing the influence of polymer-solvent interactions on the conformation and expansion of the molecules in solution, it is common to characterize a solvent as either "good", "bad" or as a "θ-solvent" for the actual polymer molecule. A good or bad solvent will cause the molecule to expand or retract with respect to excluded volume, respectively. A θ-solvent is a slightly bad solvent that causes attractive forces between segments of the polymer to accurately compensate for the fact that the real chain consists of monomers with a definite excluded volume. With polyelectrolytes with identical charges, such as those used in this study, it is of particular importance to be aware of the repulsion exerted on each other by the charged groups. In solvents of low ionic strength this repulsion causes the polyelectrolytes to assume a considerably higher expansion than can be obtained with an uncharged polymer in any solvent. However, in solvents of high ionic strength, the repulsive forces between the charges on the polyelectrolyte are shielded off, causing the molecule to collapse if the actual chain stiffness is low.

An important parameter describing a polymer molecules physical size in solution is the radius of gyration, R_G. This is defined as the distance from the centre of gravity wherein all the mass points (of the polymer segments) can be gathered without changing the molecules moment of inertia. The radius of gyration dependency on molecular weight can be shown to depend on conformation as summarized in table 2-1 below.

Table 2-1. Dependency of radius of gyration (R_G) on molecular weight (MW) for different conformations. $\propto$ symbolizes proportionality (from Smidsrød and Moe, 1995).

Conformation	**R_G dependency on MW**
Sphere	$R_G \propto \mathrm{MW}^{1/3}$
Transitional region sphere - coil (branched flexible coils)	$R_G \propto \mathrm{MW}^{0,33 - 0,5}$
Flexible coil	$R_G \propto \mathrm{MW}^{0,5 - 0,6}$
Transitional region coil - rod (rigid chains)	$R_G \propto \mathrm{MW}^{0,6 - 0,99}$
Rod	$R_G \propto \mathrm{MW}$

2.4.3 Toxicity of polymer coagulants

The work on this thesis has not included a comprehensive survey on literature regarding the toxicity of organic polymers used in water treatment practice. However, it is felt that the issue is too important to go unmentioned. The following is mainly based on a short presentation by Bolto (1995).

Cationic synthetic polymers, such as those used in this study, are generally considered to be more toxic than anionic and non-ionic polymers and the residual monomers that can be present in the products are generally more toxic than the polymers themselves (Criddle, 1990). As a result of this many countries have put strict regulations on the quality of organic polymer products for use in water treatment (especially with regards to contents of residual free monomers) as well as limitations on their use in general. The restrictions are generally more stringent with respect to cationic polyelectrolytes, some countries not permitting their use in potable water treatment at all. In Norway, limitations in the use of polymers in drinking water treatment are set both with respect to maximum allowed monomer content in the products, as well as on maximum allowed dosages of the products themselves. Bolto (1995) refers to Japan and Switzerland as examples of countries where the use of polyelectrolytes in drinking water treatment has been prohibited altogether, whereas France and Germany have stringent limits. Bolto furthermore refers to a detailed review by Letterman and Pero (1990) on the health significance of possible contaminants in polyelectrolyte products.

A major motivation behind the interest in chitosan as a coagulant in water treatment is the fact that it is a virtually non-toxic biopolymer (Aspden *et al*, 1997 and Haffejee *et al*, 2001). At present however, there are also limitation with respect to the use of chitosan as a coagulant in drinking water treatment (e.g. Norway and Germany).

2.5 Polymer induced coagulation of organic matter (NOM) in natural waters

2.5.1 Removal efficiencies

2.5.1.1 Maximum observed removal efficiencies for different polymers

An attempt has been made to survey highest observed removal efficiencies reported in different studies including coagulation of NOM using cationic polyelectrolytes as sole coagulants. The results have been categorized into polyelectrolyte types and removals with respect to frequently used colligative parameters and are presented in the table 2-2 below. Within each polymer category there may be significant differences regarding molecular weights and/or charge densities.

Table 2-2. Summary of highest reported removals of NOM with cationic polyelectrolytes as sole coagulants found in literature survey. Blank fields in the table indicate that no values are reported in the referred reference

Quaternary ammonium polyamines

Raw water	**Removal (in %) of**				**Reference**
	Colour	UVA	DOC	using a dose of	
Natural waters		51-58	37-39	5 mg/l or 1 mg/mg TOC	Edzwald *et al* (1987)
Reconstituted reverse osmosis concentrate from coloured upland water (UK)	60			4 mg/l for raw water colour 2,5 Abs (400nm)/l	Graham *et al* (1992)
Commercial humic acid (5 mg DOC/l)		90		7,5 mg/l or 1,5 mg/mg DOC	Lurie and Rebhun (1996)
Polethyleneimines (PEI)					
Commercial humic acid (5 mg/l)	98-100 (f) 85-88 (jt)			3,0 mg/l in f : depth filtration, jt : jar test experiments	Glaser and Edzwald (1979)
Reconstituted reservoir / river water (HS 60-65% of DOC)	44-61	33-49	32-35	5 mg/l or 1 mg/mg TOC	Bolto *et al* (1998)

Table 2-2, continued

Cationic polyacrylamide copolymer (CPAAM)

Raw water	**Removal (in %) of**				**Reference**
	Colour	UVA	DOC	using a dose of	
Commercial humic acid (5 mg DOC/l)		80		20 mg/l or 4 mg/mg DOC	Lurie and Rebhun, 1996
Reconstituted river water (HS 52% of DOC)		55			Bolto *et al* (1999)
Reconstituted river water (HS 65% of DOC)	67	50	57	7-8 mg/l or 1,4-1,6 mg/mg TOC	Bolto *et al* (1998)
Commercial humic acid (19,2 mg C/l DOC)		90		40 mg/l or 2,1 mg/mg DOC	Kam and Gregory (2001)
Reconstituted groundwater (HS 89% of DOC)		69			Bolto *et al* (1999)
Cationic polymethacrylate (CPMA)					
Reconstituted groundwater (HS 89% of DOC)		75			Bolto *et al* (1999)

Table 2-2, continued

Polydiallyldimethylammonium chloride (PDADMAC)

Raw water	**Removal (in %) of**				**Reference**
	Colour	UVA	DOC	using a dose of	
Reconstituted groundwater (HS 89% of DOC)		70			Bolto *et al* (1999)
Reconstituted reservoir/river water (HS 60-65% of DOC)	82-95	66-68	64-70	5-8 mg/l or 1,0-1,6 mg/mg TOC	Bolto *et al* (1998)
Reconstituted river water (HS 52% of DOC)		49			Bolto *et al* (1999)
Commercial humic acid (19,2 mg C/l DOC)		90		20 mg/l or 1,05 mg/mg DOC	Kam and Gregory (2001)
Chitosan					
Reconstituted reservoir/river water (HS 60-65% of DOC)	59-82	58-60	68-93	8 mg/l or 1,6 mg/mg TOC	Bolto *et al* (1998)
Reconstituted humic water (ion exchange regenerant)	90	-	55	7,5 mg/l or 1,36 mg/mg TOC	Eikebrokk (1999)
Reconstituted humic water (ion exchange regenerant)	82	-	40	4 mg/l or 0,73 mg/mg TOC	Saltnes (2002)

Depending on polyelectrolyte type, raw water type and treatment protocol (depth filtration vs. jar tests) the results show that with respect to colour removals from about 40% up to almost complete removal has been achieved using polyelectrolyte coagulants. With respect to UV absorbing NOM and dissolved organic carbon (DOC) removals of 33-90% and 32-93% respectively have been observed.

Generally higher removal efficiencies have been observed in NOM containing waters prepared from commercial humic salts than in natural or reconstituted natural NOM containing waters. Furthermore the results indicate that polyelectrolytes are more efficient in removing coloured substances than the bulk of NOM measured as total dissolved organic carbon. This is discussed further in chapter 2.5.3.

2.5.1.2 Studies that address direct comparisons of different polymers efficiencies

Due to the great variation in coagulability of the different raw water types and differences in experimental protocols and response variables, the survey presented above does not provide a sound basis for drawing general conclusions on what polyelectrolyte types are the more effective in coagulation of NOM containing waters. Comparisons of the efficiency of different polyelectrolyte types must therefore be based on studies testing different polyelectrolytes on the same raw water and under identical experimental conditions.

Bolto *et al* (1998) reports on two studies comparing the efficiencies of different cationic polyelectrolyte coagulants.

Table 2-3. Summary of highest observed removals of colour, UVA and TOC by coagulation with alum and different cationic polyelectrolytes in two different waters. The original results are reported in a study by Bolto *et al* (1998). The coagulants are listed in declining order with respect to their efficiency as coagulants.

Bell Bay water			**Hope Valley water**		
Colour	**UVA**	**TOC**	**Colour**	**UVA**	**TOC**
Alum (95%)	Alum (88%)	Chitosan (93%)	Alum (95%)	Alum (88%)	PDADMAC (70%)
PDADMAC (95%)	Chitosan (69%)	Alum (65%)	PDADMAC (82%)	PDADMAC (65%)	Chitosan (68%)
Chitosan (82%)	PDADMAC (68%)	PDADMAC (45%)	CPAAM (67%)	Chitosan (58%)	Alum (65%)
CPAAM (82%)	CPAAM (50%)	PEI (35%)	Chitosan (59%)	CPAAM (50%)	CPAAM (57%)
PEI (61%)	PEI (49)		PEI (44%)	PEI (33%)	PEI (32%)

Coagulation efficiencies using cationic polyacrylamide copolymer (CPAAM), poly diallyldimethylammonium chloride (PDADMAC), polyethyleneimine (PEI) and chitosan are compared with each other and with alum in experiments on reconstituted NOM containing water. This study reports on observed efficiencies with respect to colour as well as UV absorbing substances (UVA) and total organic carbon for unfractionated water as well as for four different single fractions with different hydrophobicity and charge. The experimental technique used in these studies is a traditional jar test but with filtration through paper filter as an additional particle separation step. It should be observed that the CPAAM used in this study has a high charge density (85%) and that the pH (6) under which the coagulation took place was not the most favourable with respect to the charge densities of chitosan and PEI being 40 and 67% respectively at this pH. With respect to colour removal PDADMAC is found to be the most efficient coagulant, PEI the least effective and CPAAM and chitosan quite comparable.

In a later reported study (1999) Bolto *et al* compares the efficiencies of PDADMAC, CPMA and CPAAM against each other and against alum as coagulants on three different reconstituted NOM containing waters (unfractionated as well as separate fractions). The experimental technique is the same as above and a sorted summary of the results (removal of UVA) is given in table 2-4 below.

Table 2-4. Summary of highest observed UVA-removals in a study by Bolto *et al* (1999) comparing the efficiency of cationic polymethacrylate (CPMA), PDADMAC and alum as coagulants for NOM in three different waters. The coagulants are listed in declining order with respect to their efficiencies as coagulants.

Moorabool	**Hope Valley**	**Wanneroo**
Alum (69 %)	Alum (88 %)	Alum (88 %)
CPMA (55 %)	PDADMAC (65 %)	CPMA (75%)
PDADMAC (49 %)	CPMA (50 %)	PDADMAC (70 %)
CPAAM (45 %)	CPAAM (50 %)	CPAAM (69 %)

The results reported here are for CPAAMs and CPMAs of high MW and high CD, and show that the efficiencies of the three different polyelectrolyte types are quite comparable with PDADMAC, and CPMA being in general slightly more efficient than CPAAM. The two studies by Bolto *et al* (1998 and 1999) also investigate the effect of varying MWs and CDs using a range of different PDADMACs and CPAAMs. These findings are reported in chapter 2.5.5 dealing particularly with the effect of polyelectrolyte molecular weight and charge density.

It should be noticed that the efficiency of polyelectrolytes as coagulants for NOM generally was found to be strongly dependent on the water source and the difference in character of the NOM found in these waters. These effects are reviewed in more detail in chapter 2.5.4.

Kam and Gregory (2001) investigated charge neutralisation aspects, coagulation kinetics and efficiency of twelve different cationic polyacrylamide copolymers (acrylamide (AA) and quaternized dimethyl aminoethyl acrylate (DMAEA)) on solutions of a commercial humic acid and compared them with a PDADMAC. The paper deals mainly with the effects of varying CDs and MWs (reviewed in chapter 2.5.5) but reports removals of UVA (at 300 nm) to be comparable to those of Bolto *et al* (1998) with about 90 % removal for the most highly charged AA-DMAEA (CD 2,61 meq/g) and PDADMAC (CD 5,73 meq/g).

Lurie and Rebhun (1996) compared the efficiencies in removing UVA from solutions of a commercial humic acid using a highly charged, low MW poly-Epi-amine (MW 50 000, CD 7,4 meq/g) with a low CD cationic polyacrylamide copolymer (MW 1,6 mill, CD 1,6 meq/g). Although the polyamine was found to be more efficient, the performances of the two polyelectrolytes were quite comparable, removing 90 and 80 % of UVA respectively. Another interesting observation however was that the low MW, fully charged poly Epi-amine produced small pinpoint flocs whereas the high MW, low CD cationic polyacrylamide copolymer produced large floc clusters (in addition to minute size precipitations at high dosages).

2.5.1.3 Studies that address direct comparisons of efficiencies of polymer and metal salt coagulation

Several studies have directly compared metal salt coagulants and cationic polyelectrolytes for the removal of NOM from water (Bolto *et al*, 1998 and 1999, Edzwald *et al*, 1987, Eikebrokk, 1999, Graham *et al*, 1992, Saltnes, 2002). An overview of some of the results is presented in table 2-5 below as well as in tables 2-3 and 2-4, revealing that in most cases the use of metal salt coagulants is superior to the use of cationic polyelectrolytes for removing colour as well as total dissolved organic matter from water. Filtration studies (Eikebrokk, 1999, Graham *et al*, 1992, Saltnes, 2002) however revealed that that although the use of metal salt coagulants gave higher removal efficiencies they also resulted in increased head loss development and shorter filter run times due to the production of excess particulates (metal hydroxide precipitations).

Table 2-5. Comparisons of highest observed removals of NOM found in studies particularly adressing the efficiency of polyelectrolytes relative to metal salt as coagulants for NOM

Raw water	**Highest observed removal efficiency**		**Reference**
	Polyelectrolyte	**METAL SALT COAGULANT**	
Natural waters	58 % UVA 39 % TOC	76 % UVA 57 % TOC	Edzwald *et al* (1987)
Reconstituted natural water	60 % colour	94 % colour	Graham *et al* (1992)
Reconstituted humic water (ion exchange regenerant)	90 % colour 55 % TOC	95 % colour 80 % TOC	Eikebrokk (1999)
Reconstituted humic water (ion exchange regenerant)	82 % colour 40 % TOC	95 % colour 85 % TOC	Saltnes (2002)

2.5.2 Dosage stoichiometry and mechanisms proposed for the coagulation of NOM with cationic polyelectrolytes

Coagulation (or precipitation) through charge neutralisation is by most investigators considered to be the only likely mechanism in polyelectrolyte coagulation of NOM (Edwards *et al*, 1994, Glaser and Edzwald, 1979; Narkis and Rebhun, 1977, Kam and Gregory, 2001). These conclusions are based on the findings of charge neutralisation stoichiometry between anionic charges of the humic substances and cationic charges provided by the addition of polyelectrolytes, and the lack of an effect of polyelectrolyte MW on the coagulation efficiency.

Narkis and Rebhun (1977) found a stoichiometric relationship between the concentration of humic or fulvic acids and the optimal polyelectrolyte (polyethyleneimine, MW 30 000) dosage to achieve coagulation. It was shown that the dosage stoichiometry was consistent with a charge neutralisation stoichiometry between anionic charged groups in the humic matter (phenolic and carboxylic groups) and cationic quaternary amine groups in the polyelectrolyte, expressed as opposite charge equivalents per litre solution. Kam and Gregory (2001) found for polyelectrolyte charge densities of around 3 meq/g and greater a simple 1:1 charge neutralisation stoichiometry in coagulation studies on solutions of commercial humic acid.

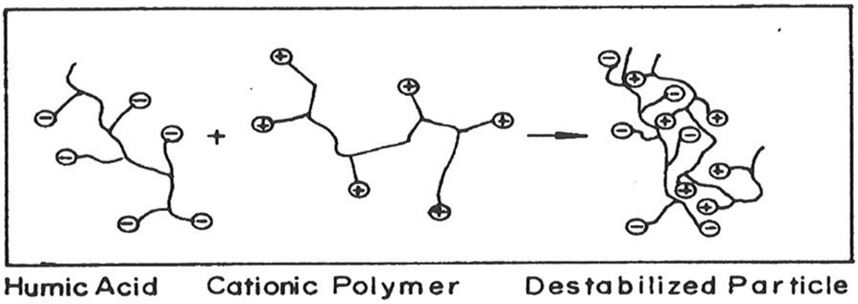
Bolto *et al* (1998) found the effect of increasing MW to be more important for colour removal than increasing charge density (see chapter 2.5.5) suggesting the presence of an inter particle bridging mechanism.

Glaser and Edzwald (1979) offers a schematic illustration of a charge neutralisation mechanism where alternating layers of polyelectrolyte molecules and humic matter form cross-linked aggregates (figure 2.9 below).

Chemical forces such as hydrogen bonds are suggested to contribute to the cross linking in addition to electrostatic forces between the opposite charges of the polyelectrolyte and humic matter. The additional effect of H-bonding is also suggested by Bolto *et al* (1998) to explain the efficiency of chitosan as a coagulant at unfavourable pH-values proposing the possibility of formation of H-bonds between unprotonated amine groups on the polyelectrolyte and the OH-groups on humic substances.

It is furthermore interesting to notice that the charge neutralisation stoichiometry between humic substances and cationic polyelectrolytes appears to depend on the charge densities of the polyelectrolyte (or the relative difference in opposite charge densities of the humic substances and the polyelectrolyte). Kam and Gregory (2001), investigating charge interaction between cationic polyelectrolytes and humic substances with four distinctively different methods, showed that for polymer charge densities of around 3 meq/g and greater a simple 1:1 charge neutralisation stoichiometry could be observed. However at lower polyelectrolyte charge densities a non-stoichiometric relationship was observed with progressively lower amounts of cationic charge needed to neutralize the anionic charge of the humic acid as the charge density of the polymers decreased. The explanation suggested is incomplete counter-ion displacement when the spacing between cationic charges along the polymer is greater than between anionic charges on the humic substance.

Initial Chemical Interaction



Floc Formation

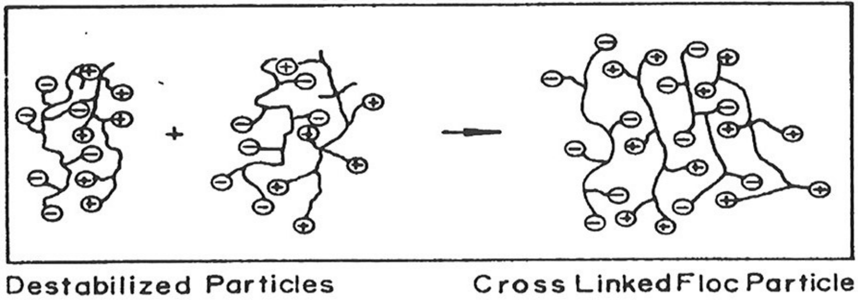


Figure 2.9. Schematic presentation of coagulation and floc formation of humic acid with cationic polymer as proposed by Glaser and Edzwald (1979)

Lurie and Rebhun (1996) report on similar findings for coagulation of solutions of commercial humic acid. Investigations into the humic substances removal efficiency as function of meq cationic charge added per litre solution revealed great differences between a fully charged, low MW poly-Epi-amine and a low CD cationic polyacrylamide copolymer. The former was found to remove 0,08 g of humic substances per meq cationic charge added, whereas the corresponding number for the latter was 0,15 g removed per meq cationic charge. In other words, the low CD cationic polyacrylamide copolymer was found to remove twice as much humic substances per meq cationic charge added as the fully charged poly-Epi-amine. The explanation suggested by the authors is that non-ionic segments of the polyacrylamide copolymer screens off up to 50% of the anionic humic charge rendering the precipitation complex with a net EPM equal to zero. This conclusion builds on the facts that the charge density of the humic substances (-6,2 meq/g), and therefore the geometric spacing between anionic charges, is much greater than the charge density of the cationic polyacrylamide copolymer (+1,6 meq/g).

2.5.3 NOM characterization and treatability

2.5.3.1 Treatability of different NOM fractions (humic / non-humic)

Several investigators have demonstrated the susceptibility of NOM to be coagulated with polyelectrolytes to increase with increasing hydrophobicity of the NOM (Amy and Chadik, 1983, Bolto *et al*, 1998 and 1999). Similar trends have been reported for inorganic coagulants (Edzwald *et al*, 1985, 1987, Owen *et al*, 1995).

Bolto et al (1998) studied the coagulation of separate NOM fractions with varying hydrophobicity using alum and different cationic polyelectrolytes (PDADMAC, chitosan, polyethyleneimine and cationic polyacrylamide copolymer). Best removal efficiency with regards to TOC and UVA was observed for the strongly hydrophobic fractions (humic acids), independent of coagulant, followed by comparable efficiency for the weakly hydrophobic (fulvic acids) and anionic hydrophilic fractions (proteins, etc.). The authors refer to similar findings by Levine *et al* (1996). Removal of UV absorbers from the neutral hydrophilic fractions was poor, but with regards to TOC, removals up to 45% were observed using chitosan. Comparison of coagulation results for unfractionated, whole waters versus the different fractions seemed to indicate that the different fractions might stabilize each other in the whole water. In a similar study reported in 1999 by Bolto *et al*, the same dependence of coagulability on the net hydrophobicity of NOM (related to % hydrophobic humic acids of total NOM) is demonstrated for polyelectrolyte coagulants as well as alum.

For dissolved humic substances (humic and fulvic acids) the differences in coagulability is frequently also attributed to differences in functional (acidic) groups content, explaining the higher coagulability of humic acids over fulvic acids with a lower content of carboxylic and phenolic groups and thus lower anionic charge to be neutralized (Amy and Chadik, 1983; Owen *et al*, 1995). In Amy and Chadik (1983) it is shown clearly that the higher coagulability of humic over fulvic acids relates both to dose efficiency of the polyelectrolyte (amount coagulated per mg of polyelectrolyte added) and highest obtainable degree of coagulation. With respect to dose efficiency these findings are consistent with the charge neutralization stoichiometry observed in coagulation of humic substances with cationic polyelectrolytes.

2.5.3.2 Treatability dependence on NOM MW

The treatability of NOM containing waters has also been shown to depend on the molecular weight distributions of the NOM. Using alum Edwards *et al* (1994) and Owen *et al* (1995) found the precipitability of NOM to increase with increasing molecular weight. Owen *et al* (1995) also found the fractions of NOM with relatively higher MW to account for the majority of UV absorbing constituents, and preferential removal of UVA over DOC using alum, whereas the lower MW fractions were found to be dominating for THMFP.

2.5.4 The effect of polyelectrolyte characteristics; charge density and molecular weight

In order to explain the performance of different polymers with regards to NOM removal much effort has been put into relating performance to general polymer characteristics such as charge density and molecular weight. Differences in observed efficiency as coagulants for NOM have also been suggested to be related to differences in polyelectrolyte main chain hydrophobicity (Bolto *et al*, 1998), efficiency increasing with increasing hydrophobicity, but no reports have been found that specifically addresses this issue.

2.5.4.1 Charge density

In accordance with the observed charge neutralisation stoichiometry for polyelectrolyte coagulation of NOM (see chapter 2.5.3) there appears to exist a general agreement on that the effectiveness of polyelectrolytes as coagulants for NOM increases with increasing charge density (Bolto *et al*, 1999; Kam and Gregory, 2001). Kam and Gregory (2001) studied coagulation kinetics and colour removal from solutions of commercial humic acid using an assortment of cationic polyacrylamide copolymers with varying charge density. Both dose efficiency and highest observed removal of colour were found to increase with increasing cationic charge density from around 0,7 meq/g up to 3 meq/g. As mentioned in chapter 2.5.2 it was found that at charge densities below 3 meq/g the polyelectrolytes exhibited increasing cationic charge dose efficiency with decreasing charge density. Increasing charge density from 3 meq/g up to 5,7 meq/g gave no further improvement with respect to highest observed removals. It was also shown that the dosage range for good removal becomes narrower as the charge density of the polymers increases. Bolto *et al* (1999) reports similar findings comparing the effectiveness of two cationic polyacrylamide copolymers with low and high charge densities.

2.5.4.2 Molecular weight

Reports on the effects of polyelectrolyte MW on their effectiveness for removal of NOM are more contradictory. Kam and Gregory (2001) directly comparing a range of cationic polyacrylamide copolymers with MW from 2 to 15 million observed no effects of MW on coagulation kinetics or colour removal. Amy and Chadik (1983) observed no beneficiary effects on THMFP-removal from increased MW for low and medium MW quaternary ammonium polymers. On the contrary, low MW quaternary ammonium polymers generally performed better than corresponding medium MW polymers.

On the other hand, Bolto *et al* (1998) found the effect of increasing MW to be more important for colour removal than increasing charge density. A CPAAM with MW of 5 million and charge density of 63% performed better than a CPAAM with MW of 2 million and charge density of 81%. For PDADMACs a significant improvement in colour removal performance was observed when increasing MW from 250 000 to 500 000. The authors suggest that the effect can be explained by bridging mechanism coagulation in addition to charge neutralisation.

Glaser and Edzwald (1979) observed no effects of MW with regards to removals or optimal polymer dose comparing polethyleneimines with MWs of 60 000 and 50 000-100 000 in depth-filtration experiments on commercial humic acid solutions. However, higher head loss development was noted for the low MW polyethyleneimine. This was explained assuming that the lower MW polyelectrolyte produced aggregates of lower physical strength. With a flocculation period prior to filtration, filtration efficiencies improved with increasing MW of the polyelectrolyte. This was attributed to the capability of the higher MW polyelectrolyte to produce larger and stronger flocs than the low MW polyelectrolyte.

2.5.5 The effect of solvent (water) pH and ionic strength

2.5.5.1 pH

Solution pH affects the coagulation of NOM by influencing the anionic charge density (ionisation of functional groups) and solubility of the NOM and by influencing the charge density of weakly basic polycations such as chitosan and partly quaternized polyethyleneimine. Several experimenters have found that the coagulation of NOM by polyelectrolytes is favoured by a reduction in pH, with respect to highest obtainable removals of NOM as well polyelectrolyte dose efficiency.

In pilot plant direct filtration experiments on natural waters using high charge density, low MW cationic polyelectrolytes Edzwald *et al* (1987) found that removal of UVA and TOC at optimal dosage was improved by lowering of the coagulation pH from 6,7-7,5 to 5,3-6,4. The effect of pH on dosage demand was not discussed. Amy and Chadik (1983), using low and medium MW cationic polyelectrolytes for coagulation of NOM containing waters from 7 different sources, observed that adjusting the coagulation pH from ambient (6,5 - 8,5) to pH 6 had a positive effect on THMFP-removal, probably due to lowered charge densities of the NOM, and resulting in 25 – 50 % reductions in polyelectrolyte dosage demands. Also, better performances were observed for waters with low ambient pH (6,5) than for waters with higher ambient pH (8,5).

Narkis and Rebhun (1977) also found that decreasing solution pH resulted in improved coagulation of solutions of humic and fulvic acids at lower dosages of polyethyleneimine. This is by the authors attributed mainly to the charge neutralization stoichiometry in that lower pH values results in lower degree of dissociation of humic and fulvic anionic functional groups (phenolic and carboxylic), in other words lower charge density of the humic matter, again resulting in a lower demand for opposite charge (polyelectrolyte) to achieve charge neutralization. The same effect is used to explain that the dosage range of polyelectrolyte in mg/l for good clarification becomes narrower as solution pH decreases. It is also pointed out that the reduced degree of dissociation of anionic functional groups in the humic matter reduces the solubility and increases the hydrophobicity of the humic matter, thus thermodynamically favouring its precipitation from solution. It is however unclear from the report whether the polyethyleneimine used in the study is fully quaternized or only partly quaternized (with pH-dependent charge density).

Levine *et al* (1996), using a combination of 1,5 mg/l PDADMAC and 20 mg/l alum, observed the removal of nonpurgeable organic carbon (NPOC) to be best at low pH (6 compared to 7 and 8) and that the removal of the hydrophilic NPOC fraction was influenced to a greater degree by pH adjustment (reduction) than the hydrophobic fraction.

Bolto *et al* (2001) however reports findings that in part contradict the findings described above. In this study on different fractions of NOM, increasing pH from 4,5 to 7,0 lead to an increase in removal of colour and UVA from 50 to 86% and 42 to 55% respectively for coagulation of the VHA fraction (very hydrophobic acids, ascribed to humic acids) using PDADMAC as the coagulant. Required dose was found to increase only slightly, from 3,0 to 3,1 mg/l. The authors consider the explanation of this to be that the pH-promoted increase in charge density on the humic substances renders them more easily complexed by the polyelectrolyte.

In the case of a weak polycation such as chitosan the effect of pH on the removal of colour and UVA was by the same authors found to be dominated by the characteristic weak basicity of the polyelectrolytes. Increasing pH from 4,5 to 7,0 leads to a reduction in charge density in the current chitosan from 98 to 17%. This again leads to an increase in optimum polyelectrolyte dose from 1,5 to 2,2 mg/l and a reduction in colour removal from 100 to 60%. The decrease in UVA removal dose efficiency is somewhat less pronounced. The negative effect of increasing pH on dose efficiency for chitosan is suggested to a certain extent to be counteracted by the possibility of formation of hydrogen-bonds (H-bonds) between the humic acids and the chitosan. It should also be noted that the authors explain the higher removal at pH 4,5 with an increased possibility for H-bond formation between undissociated carboxyl groups on the humic acids and hydroxyl groups on chitosan. This hypothesis appears however to be in contradiction to a previously proposed mechanism of H-bond formation proposed by the same authors in the 1998-paper where they propose formation of H-bonds between unprotonated amino groups on the chitosan and hydroxyl groups on the NOM, thus explaining an unexpected good efficiency of chitosan at near neutral pH.

2.5.5.2 Ionic strength

It is plausible to assume that the ionic strength of the water has a significant effect on coagulation of NOM by polyelectrolytes, as it has on destabilisation of charged particles. Regrettably an attempt to find literature addressing this issue specifically for NOM-polyelectrolyte systems failed. From more general literature it can however shortly be pointed out that ionic strength strongly influences several aspects of the NOM-polyelectrolyte system, such as:

- The thickness of the electrical double layer surrounding charged macromolecules in solution (Tanford, 1961)
- Polyelectrolyte conformation and expansion in solution (Smidsrød and Moe, 1995)
- Flocculation rate in case of electrostatic patch effects between NOM-polyelectrolyte aggregates (Gregory, 1973)
- Ionisation of weakly charged polyelectrolytes such as chitosan (Smidsrød and Moe, 1995)
- Entropy gain from release of counter ions from interacting oppositely charged macromolecules (Piculell and Lindman, 1992)

Undoubtedly the effect of ionic strength on the interaction between NOM and polyelectrolyte coagulants constitutes a very interesting field for extensive discussion and study, perhaps most of all to shed new light on the mechanisms involved. It has however not been an ambition in this study to specifically address this and further elaborations on the subject will therefore not be carried out here.

2.5.6 The effect of inorganic particles

Several investigators have found that the presence of inorganic particles (mineral or *in situ* formed metal hydroxides) has beneficiary effects on the removal of NOM using polyelectrolyte coagulants. These effects may be attributed to the particles acting as adsorbents for NOM, providing nuclei for coagulation of dissolved NOM as well improved conditions for flocculation due to increased total particle concentration. The effects of using metal salt coagulants in combination with cationic polyelectrolyte coagulants are treated separately in chapter 2.5.7.

Positive effects of the presence of mineral (in most cases clay) particles on the removal of NOM with polyelectrolytes have been observed in cases where particles have been added in the treatment process but also in cases where the particles occur naturally in the water.

Amy and Chadik (1983), using low and medium MW cationic polyelectrolytes for coagulation of natural NOM and particle containing waters (turbidity ranging from 0,37 to 63 NTU) from 7 different sources found waters with low turbidity (2,3 and 3,6 NTU) to be more amenable to polymer coagulation than waters with moderate or high (> 17 NTU), or virtually no turbidity (0,37 and 0,42 NTU). In coagulation experiments on NOM containing waters prepared from commercial humic and fulvic acids, addition of kaolinite (50 mg/l) was found to enhance polymer coagulation efficiency with respect to THMFP-removal, kaolinite particles assumed to be providing nuclei for floc formation.

Bolto *et al* (1998) observed that addition mineral particles (20 mg/l) resulted in improved colour removal from reconstituted NOM containing waters using CPAAM and PDADMAC as coagulants. The beneficial effect of adding particles appeared to be dependent of particle sizes, smaller particles showing a more pronounced effect than larger particles (actual particle sizes not specified). The effect was not as pronounced with respect to removal of UV-absorbance.

Bolto *et al* (1998) (referring to Kancharla *et al*, 1997 and Murcott and Harleman, 1993) suggest that the addition of clay causes most of the organic (humic) material to adsorb on the particle surface, thereby converting the NOM to an insoluble form. The NOM covered particles can then be coagulated/flocculated by addition of cationic polyelectrolytes. The mechanism is proposed (Kaiser and Zech, 1998) to be a ligand exchange between carboxylate groups on the NOM and hydroxyl groups bound to a polyvalent metal on the clay surface:

$$>\text{M-OH} + \text{RCOO}^- \quad \rightarrow \quad >\text{M-OOR} + \text{OH}^-$$

The affinity for humic substances increases with increasing metal content of the surface, causing for instance metal oxides to adsorb humic acid more strongly than clays.

2.5.7 Polymer – metal salt combinations

When metal salt coagulants are added to water a series of chemical reactions occur which open for a variety of possible interactions with NOM. These reactions and interaction themselves constitute their own complex and extensive field of science. Although a good understanding of this is necessary to fully understand what happens when metal salt coagulants are used in combination with cationic polyelectrolytes to coagulate NOM, it is not the ambition of this work to elaborate too much on this issue. Good general introductions to this field of chemistry are found in most textbooks on water treatment and water chemistry and will not be repeated here. A short summary of the most important aspects involved is however in place.

Metal salts coagulants, such as iron chloride sulphate, act as acids when added to water, forming a series soluble hydrolysis products, of which many are positively charged, as well as hydroxide precipitates, depending on pH and total concentration of the metal salt. Metal salt induced coagulation of NOM is believed to include three major mechanisms; charge neutralisation of anionic functional groups on NOM with positively charged free metal ions or hydrolysis products, enmeshment of NOM in metal hydroxide precipitates and adsorption of NOM to the same. Again the dominating mechanism depends on pH and metal salt dose.

Investigations specifically addressing the combined use of metal salt coagulants with cationic polymer coagulants do not offer totally unanimous findings. Graham *et al* (1992) could in filtration experiments with combinations of aluminium sulphate and a cationic polyamine Magnafloc LT31 (as well as the to coagulants alone) not demonstrate any synergistic effects. On the contrary the best filter performance was observed using alum as sole coagulant. Partial replacement of alum with polymer resulted in increasingly less effective coagulation of colour and diminishing filter performance.

On the other hand, Bolto *et al* (1999) found that combined use of alum and PDADMAC as coagulants in jar test experiments (with paper/membrane filtration as particle separation) on reconstituted NOM containing waters (reverse osmosis and magnetic ion exchange) had a synergistic effect on NOM removal, resulting in decreased dosages of alum and polymer (alum dosage reduced from 30 to 10 mg/l in presence of 0,5 mg/l PDADMAC). James and O'Melia (1982) made similar observations in jar test experiments on lake water with high contents of turbidity as well as TOC (turbidity 28 NTU, TOC 9 mg/l).

Combination of alum and a high MW, low CD polymer produced the most effective removals of TOC (and turbidity) compared to the use of alum and respectively a low MW, high CD and high MW, low CD polymer alone and a combination of alum and the low MW polymer. When used in combination the best results were obtained by adding alum first, followed by the polymer.

2.6 Polymer induced coagulation in municipal wastewater

Research on the use of cationic polyelectrolytes as coagulants in wastewater systems has more or less exclusively been focused on the removal of particulate matter. A few investigators have observed and commented on the coagulation of dissolved organic matter as a side effect to the coagulation and flocculation of particles, but the search on reports focusing on the coagulation of dissolved organic matter itself in sewage systems has been unsuccessful. Neither has the search for studies on characterisation of dissolved organic matter in wastewater with respect to its coagulability. Reports on the characterisation of organic matter in municipal wastewater have mainly concerned themselves with biodegradability and particle size distributions, motivated by the need for knowledge related to biological treatments protocols and the removal of particulate matter.

2.6.1 Dissolved organic matter in municipal wastewater

The division between dissolved and particulate matter in wastewater (and natural waters) is in the context of water treatment operationally defined as matter respectively passing or being withheld by a certain filter pore size. The actual filter pore size chosen to separate dissolved from particulate matter varies somewhat in different studies, but is normally found between 0,025 and 1,0 μm.

With respect to biological wastewater characterisation for the IAWQ ASM, a separation diameter of 0,45 μm has been applied to distinguish between dissolved and particulate matter (Henze, 1992).

Nieuwenhuijzen (2002) recently published a survey on the particle size distribution of organic matter in wastewater. With references to investigations conducted in different European countries and the USA it is concluded that the major part of organic matter in municipal wastewaters is related to particles. Local variation is substantial, but on average it was found that about 30% of COD is present in the, again operationally defined, soluble form. In his own particle size fractionation experiments Nieuwenhuijzen (2002) found that filtration through 0,45 µm on average overestimated the dissolved fraction of COD by 8% relative to filtration through 0,1 µm. It was therefore recommended to use 0,1 µm as separation diameter in order to obtain a more correct estimates of the soluble fraction of wastewater COD.

References to investigations specifically addressing polymer coagulation of the dissolved fraction of organic substances in wastewater have, as mentioned above, not been found. However, recent reports on characterisation of dissolved organic substances in wastewater treatment plant effluents (Imai *et al*, 2002 and Namour and Müller, 1998) show substantial (up to 28 and 77 % of DOC respectively) hydrophobic fractions ascribed to UV-absorbing humic substances. Although it is shown that the hydrophobic fraction increases as result of biological degradation of the organic matter, it seems plausible to assume that also a substantial fraction of the dissolved organic matter in the influent to a wastewater treatment plant has hydrophobic, humic like characteristics, probably contributing largely to the so called biologically inert fraction of COD.

2.6.2 Coagulation of dissolved organic matter in wastewater with organic polymers

No references have been found specifically addressing the coagulation of dissolved organic matter in wastewater with organic polymers. There is of course a good reason for this as the accepted strategy for wastewater treatment is to remove the dissolved organic matter biologically and efforts with respect to polymer coagulation and flocculation have been focused on the removal of the particle fraction.

Some investigators have however observed interactions between dissolved organic matter and cationic polyelectrolyte coagulants in studies focusing on the coagulation of particles. In flocculation experiments on secondary effluents with a cationic polyelectrolyte (Purifloc C-31, no further descriptions given) Narkis and Rebhun (1996) observed initial increases in turbidity at low doses of polymer (up to 20 mg/l). These findings were ascribed to interactions between the cationic polyelectrolyte and anionic macromolecules in the effluent, forming colloidal precipitates. First at higher dosages (25 mg/l) acceptable flocculation and net decreases in turbidity after sedimentation were observed.

Lurie and Rebhun (1996) investigated flocculation of activated sludge solids in the presence of added commercial humic acids with a low MW (50 000), high CD poly Epi-amine and a high MW (6,1 mill), low CD cationic polyacrylamide copolymer. At low dosages the low MW, fully charged polyelectrolyte interacted with the humic acids causing aggregation as indicated by increase in turbidity, but no flocculation of activated sludge solids occurred. Good flocculation was achieved first at higher dosages (6 – 12 mg/l).

This initial precipitation of humics and poor flocculation was not observed for the high MW, low CD cationic polyacrylamide copolymer. The latter instead caused immediate flocculation of activated sludge even at low dosages. The authors report that these findings are in good correlation with previous results obtained by Narkis and Rebhun (1977, 1996).

2.7 Summary of main findings from the literature study

Natural organic matter (NOM) in water is generally divided into humic substances and non-humic material. Humic substances are generally hydrophobic, ill-defined complex macromolecules and constitute the main source of the yellowish-brownish colour in many natural waters (Jones and Bryan, 1998; Owen *et al*, 1995). Non-humic materials generally are less hydrophobic, more easily defined and colourless molecules such as proteins, polysaccharides, nucleic acids and small molecules such as sugars and amino acids (Jones and Bryan, 1998; Owen *et al*, 1995).

The relative proportions of humin and humic and fulvic acids (constituting the humic material) found in natural waters are site-specific and amount to, in sum, approximately 35-70 % of total organic carbon, TOC (Thorsen, 1999).

The content of ionisable functional groups such as carboxyl influences the solubility of humic substances (Owen *et al*, 1995, referring to Perdue, 1985) as well as their charge density. The pK_a of humic carboxyl groups have values between 4 and 6 (Stumm and Morgan, 1996) rendering humic substances negatively charged at pH values found in most natural waters.

Several investigators have demonstrated the susceptibility of NOM to be coagulated with polyelectrolytes to increase with increasing hydrophobicity of the NOM (Amy and Chadik, 1983, Bolto *et al*, 1998 and 1999). Similar trends have been reported for inorganic coagulants (Edzwald *et al*, 1985, 1987, Owen *et al*, 1995).

For dissolved humic substances (humic and fulvic acids) the differences in coagulability is frequently also attributed to differences in functional (acidic) groups content. In this line of reasoning, the higher coagulability of humic acids over fulvic acids has been explained with a lower content of carboxylic and phenolic groups (and thus lower anionic charge to be neutralized) in humic than in fulvic acids (Amy and Chadik, 1983; Owen *et al*, 1995).

Relativey few studies have been found comparing a broad range of different cationic olyelectrolytes as coagulants for NOM. Bolto *et al* (1998) reports on two studies comparing the efficiencies of cationic polyacrylamide copolymer (CPAAM), polydiallyldimethylammonium chloride (PDADMAC), polyethyleneimine (PEI) and chitosan in experiments on reconstituted NOM containing water at pH 6. With respect to colour, PDADMAC was found to be give the highest removals (82-95%), PEI the lowest (44-61%) with chitosan and CPAAM in between (59-82%).

Coagulation (or precipitation) through charge neutralisation is by most investigators considered to be the only likely mechanism in polyelectrolyte coagulation of NOM (Edwards *et al*, 1994, Glaser and Edzwald, 1979; Narkis and Rebhun, 1977, Kam and Gregory, 2001). These conclusions are based on the findings of charge neutralisation stoichiometry between anionic charges of the humic substances and cationic charges provided by the addition of polyelectrolytes. In accordance with this, there appears to exist a general agreement on that the effectiveness of polyelectrolytes as coagulants for NOM increases with increasing charge densities (Bolto *et al*, 1999; Kam and Gregory, 2001). However, this conclusion has mainly been based on investigations on the effect of charge density within a single polyelectrolyte type. Studies specifically addressing the effect of charge density relative to the effect of differences in chemical composition for different polyelectrolyte types have not been found.

Reports on the effects of polyelectrolyte MW on their effectiveness for removal of NOM are more contradictory. Kam and Gregory (2001) directly comparing a range of cationic polyacrylamide copolymers with MW from 2 to 15 million observed no effects of MW on coagulation kinetics or colour removal. On the other hand, Bolto *et al* (1998) found the effect of increasing MW to be more important for colour removal than increasing charge density.

Solution pH affects the coagulation of NOM by influencing the anionic charge density (ionisation of functional groups) and solubility of the NOM, and by influencing the charge density of weakly basic polycations such as chitosan and partly quaternized polyethyleneimine. Several experimenters have found that the coagulation of NOM by polyelectrolytes is favoured by a reduction in pH, with respect to highest obtainable removals of NOM as well polyelectrolyte dose efficiency (Edzwald *et al*, 1987, Narkis and Rebhun, 1977, Levine *et al* 1996).

Bolto *et al* (2001) however report findings that in part contradict these findings. In a study on different fractions of NOM, increasing pH from 4,5 to 7,0 lead to an increase in removal of colour 50 to 86% for coagulation of humic and fulvic acids with PDADMAC. Required dose was found to increase only slightly, from 3,0 to 3,1 mg/l. The authors consider the explanation of this to be that the pH-promoted increase in charge density on the humic substances renders them more easily complexed by the polyelectrolyte. In the case of a weak polycation such as chitosan the effect of pH on the removal of colour and UVA was by the same authors found to be dominated by the characteristic weak basicity of the polyelectrolytes. Increasing pH from 4,5 to 7,0 lead to an increase in optimum polyelectrolyte dose from 1,5 to 2,2 mg/l and a reduction in colour removal from 100 to 60%.

Several investigators have found that the presence of inorganic particles (mineral or *in situ* formed metal hydroxides) has beneficiary effects on the removal of NOM using polyelectrolyte coagulants (Amy and Chadik, 1983, Bolto *et al*, 1998). Positive effects of the presence of mineral (in most cases clay) particles on the removal of NOM with polyelectrolytes have been observed in cases where particles have been added in the treatment process, but also in cases where the particles occur naturally in the water.

Investigations specifically addressing the combined use of metal salt coagulants with cationic polymer coagulants do not offer totally unanimous findings. Graham *et al* (1992) could in filtration experiments with combinations of aluminium sulphate and a cationic polyamine not demonstrate any synergistic effects. On the contrary the best filter performance was observed using alum as sole coagulant. On the other hand, Bolto *et al* (1999) found that combined use of alum and PDADMAC as coagulants in jar test experiments had a synergistic effect on NOM removal, resulting in decreased dosages of alum and polymer.

James and O'Melia (1982) made similar observations in jar test experiments on lake water with high contents of turbidity as well as TOC.

Recent reports on characterisation of dissolved organic substances in wastewater treatment plant effluents (Imai *et al*, 2002 and Namour and Müller, 1998) show substantial (up to 28 and 77 % of DOC respectively) hydrophobic fractions ascribed to UV-absorbing humic substances. It seems plausible to assume that also in the influent to a wastewater treatment plant a substantial fraction of the dissolved organic matter has hydrophobic, humic like characteristics, probably contributing largely to the so called biologically inert fraction of COD.

Research on the use of cationic polyelectrolytes as coagulants in wastewater systems has more or less exclusively been focused on the removal of particulate matter. No references have been found specifically addressing the coagulation of dissolved organic matter in wastewater with organic polymers. Some investigators have however made notices of observed interactions between dissolved organic matter and cationic polyelectrolyte coagulants intended for the coagulation of particles. In flocculation experiments on secondary effluents with a cationic polyelectrolyte Narkis and Rebhun (1996) observed initial increases in turbidity at low doses of polymer (up to 20 mg/l). These findings were ascribed to interactions between the cationic polyelectrolyte and anionic macromolecules in the effluent, forming colloidal precipitates. First at higher dosages (25 mg/l) acceptable flocculation and net decreases in turbidity after sedimentation were observed.

3 RATIONALE AND HYPOTHESES

As mentioned in the introduction, the coagulating agents most frequently used for coagulation of dissolved organic substances in water are inorganic salts of iron (Fe^{3+}) and aluminium (Al^{3+}). The primary use of organic polymers has been and still is as flocculating agents for already coagulated aggregates. However in the recent years the use of cationic organic polymers have received increasing attention as coagulating agents, used alone or in combination with the traditional metal salt coagulants. The interest for using organic polymers as coagulants has mainly been motivated by the fact that they do not react with, and alter the chemical properties of, the water itself to the same extent as metal salt coagulants. They do not alter pH and alkalinity of the water, add substantially less to the total ion content of the water, nor do they form large amounts of inorganic precipitates, which is the case with metal salt coagulants. Thus, sludge formation is substantially lower and with a lower water content with cationic polyelectrolyte coagulants than with metal salts, allowing for longer filter run times in depth filtration processes and lower sludge handling costs in general.

The main objective of this work has been to determine how organic cationic polymers can coagulate dissolved organic substances in water.

Although significant knowledge on coagulation of dissolved organic substances by polyelectrolytes has been achieved, it appears still to be some aspects that are poorly described and understood:

- There are few comprehensive studies comparing a broad range of different polyelectrolyte types thereby describing the effects of differences in chemical composition relative to those of differences in charge density
- The relationship between the coagulation or precipitation of the dissolved organic substances and the following flocculation of the aggregates appears to be poorly understood
- It appears to be unclear whether the reported effects of polyelectrolyte charge density can be ascribed to the actual spatial distribution of charge along the polymer backbone as such or whether they are merely effects of different additions charge equivalents occurring when adding equal amounts of polyelectrolytes with different charge densities
- Few, if any, studies have been reported specifically addressing the coagulation of dissolved organic substances with polymers in

wastewater. Accordingly few attempts have been made to investigate differences and similarities of the coagulation processes as they occur in two widely different systems as wastewater and humic surface water

It follows from this that in the practical realisation of the main objective three dimensions can be identified along which sub objectives and practical choices have been formulated. These are related to

- Experimental methodology and design
- Choice of polymers for testing
- Choice of raw waters

In the choice of experimental methodology the main objective has been to study the coagulation process (of dissolved organic substances) as such, disconnecting the obtained results from dependency on floc growth and separability of formed flocs, or the floc separation process, that follows the actual destabilisation and coagulation. The main objective of the experimental design was to compare coagulation efficiencies and performance of cationic polyelectrolyte coagulants over a broad dosage range, regardless of economical concerns, ranging from sub optimal to overdosage (if obtainable). In addition some sub-objectives were formulated. These were to study floc growth of aggregates, to study coagulation of particulate organic matter occurring parallel to coagulation of dissolved matter (and vice versa) and to relate results from the chosen experimental particle separation method to other, more realistic separation methods (filtration, sedimentation, dissolved air flotation).

The main objective in the choice of polymers for testing was to achieve a comprehensive direct parallel comparison of a wide spectrum of different cationic polyelectrolyte coagulants, with emphasis on cationic and coagulant, covering a broad variation in chemical structure and charge density within the range of commonly used and commercially available product types. By choosing polyelectrolyte coagulants of differing charge densities as well as chemical composition it was hoped that strong individual effects of these, if at all existent, might be distinguishable. It was of special interest to compare the performance of chitosan, being a non-toxic biopolymer, to that of synthetic cationic polyelectrolytes. Furthermore it was of special interest to determine possible effects of the degree of acetylation F_A in chitosans. The common alternative to polyelectrolytes as coagulants are metal (aluminium- or iron-) salts. It was therefore decided that the results obtained with polyelectrolytes would need to be compared to results obtainable with a metal salt coagulant under the same experimental methodology.

Testing of the effect of polymer molecular weight on coagulation of dissolved organic matter was not included in the main objectives underlying the choice of polymers. The reason for was the lack of effect of this variable found by most other investigators in previous work (see literature study). However, one investigator (Bolto *et al*, 1998) found strong indications of the opposite and therefore one of the sub-objectives formulated was to test the effect of a leap in molecular weight for polyacrylamides with more or less identical charge densities (LMW vs. MMW CPAAM). In addition, studying the effect of varying degree of acetylation (F_A) in chitosans and the effect of combining use of inorganic and organic coagulants were also formulated as sub-objectives regarding choice and testing of coagulants.

The main intention in the choice of different raw water types has been to investigate the interaction of cationic polyelectrolytes with different kinds of dissolved organic substances and under different conditions. More specifically the objectives with respect to choice of raw waters have been, first, to study coagulation of humic substances in a relatively homogenous and particle free water as such, and second to investigate how the same polymers interact with humic as well as non-humic dissolved organic substances in a more heterogeneous, with respect to the composition the dissolved organic matter, and particle rich water.

Based on the findings in the literature study it was expected that pH would have significant influence on the charge density and coagulability of especially humic dissolved substances, as well as on the charge density and probably coagulant efficiency of weak polycations such as chitosan. For the sake of comparability it was therefore decided not to run experiments at ambient raw water pH, but to adjust pH of the different raw waters (and raw water batches) to a value of 6,0 prior to coagulation. However it was defined as a sub-objective to investigate the influence of coagulation pH on the performance of selected polymers. This was considered to be of particular importance with respect to chitosan, being a weak polycation.

3.1 Hypotheses

The following hypotheses were formulated to further specify the main issues to be investigated in this study:

A The relationship between coagulation of dissolved organic substances and flocculation of aggregates

Coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima. That is, the polyelectrolyte dosage providing maximal coagulation of dissolved organic substances is not identical to the dosage providing aggregates with the best flocculation properties.

B Differences in the polyelectrolytes efficiencies as coagulants for dissolved organic substances

Differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain.

C The nature of the effect of polyelectrolyte charge density on coagulation of dissolved organic substances

With respect to coagulation of dissolved humic substances the effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such.

D The effect of polyelectrolyte molecular weight on coagulation of dissolved organic substances

Differences in molecular weight have a subordinate, if any, effect on the coagulation of dissolved organic substances.

E The effect of pH on coagulation of dissolved humic substances with cationic polyelectrolytes

1) Due to increased protonation of the carboxyl groups, and thus reduced anionic charge density, of the humic substances, lowering of pH from 6 to 4 results in improved dose efficiencies with respect to coagulation of NOM with cationic polyelectrolytes.

2) With chitosan a reduction of pH will also result in a gain in cationic charge density due to protonation of the amine groups. Therefore the effect of reducing pH on polymer dose efficiency will be more pronounced for a weak polycation such as chitosan than for a strong polycation such as PDADMAC.

F Combination of metal salt and cationic polyelectrolytes as coagulants for dissolved organic substances

The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.

G The relationship between polyelectrolyte coagulation of dissolved organic substances in humic water and wastewater

A significant portion of the dissolved organic substances in wastewater is made up of humic-like substances and the coagulation of these by polyelectrolytes can be explained accordingly to that of humic substances in surface water.

4 MATERIALS AND METHODS

4.1 Coagulants

Descriptions of the polyelectrolytes coagulants used in the main experiments and additional experiments to test effects of solution pH and degree of acetylation in chitosan are presented in table 4-1.

Table 4-1. Cationic polyelectrolyte coagulants used in main frame (and some additional) experiments.

Product name (Manufacturer)	**Type**	**Molecular weight (g/mol)**	**Charge density (meq/g)**
ChitoClear (Primex)	Chitosan (degree of acetylation F_A 0,05)	80 000	4,5 (pH 6)
(Pronova Biopolymer)	Chitosan (degree of acetylation F_A 0,37)	145 000	2,4 (pH 6)
C-581 (Cytec)	Poly-Epi-amine	300 000	7,0
C-591 (Cytec)	Polydiallyldimethylammonium chloride (PDADMAC)	300 000	6,2
Fennofix 240 (Kemira)	Cationic polyacrylamide copolymer Low molecular weight (LMW CPAAM)	300 000	4,2
Fennopol K1912 (Kemira)	Cationic polyacrylamide copolymer Medium molecular weight (MMW CPAAM)	4 000 000	4,0

All specifications are as provided by manufacturer and have not been tested independently. Molecular weights given should be considered as approximate. Charge densities of chitosans are dependent on solution pH and have been calculated according to procedure given in appendix A.

All polyelectrolytes in table 4-1 are commercial products, however the two brands of chitosans are no longer in production. Chitosan with F_A 0,37, kindly provided by NOBIPOL (Norwegian Biopolymer Laboratory) at the Institute of biotechnology, NTNU, had been transferred to the chloride form prior to use. The PDADMAC, LMW CPAAM and poly-Epi-amine are delivered as solutions with active substance contents of 20% (C-591), 26% (Fennofix 240) and 50% (C-581). Chitosans and MMW CPAAM (Fennopol K1912) are delivered as solid substances (100 % active substance contents).

A set of experimental cationic polyacrylamide copolymers used in dissolved air flotation experiments on wastewater was kindly provided by Kemira. The test set was designed to independently span out variation in molecular weights and charge density as specified in table 4-2.

Table 4-2. Kemira cationic polyacrylamide copolymer testset used in batch flotation experiments on wastewater

Product code	Molecular weight (g/mol)	Charge density (meq/g)
3674.3	4 000 000	3,0
3677.2	4 000 000	3,5
3676.3	4 000 000	4,0
3674.2	5 000 000	3,0
3675.1	5 000 000	3,5
3676.1	5 000 000	4,0
3674.1	6 000 000	3,0
3677.1	6 000 000	3,5
3678.1	6 000 000	4,0

As in table 4-1 all specifications are as provided by manufacturer and molecular weights given should be considered as approximate.

In coagulation experiments including the use of iron chloride sulphate the product used was JKL (Kemira) with the following characteristics:

Formula:	$FeClSO_4$
Active substance as Fe^{3+}:	11,6 ± 0,3 % 2,07 mol/kg
Free acid, max:	20 g/kg
Sulphate, max:	230 g/kg
Chloride, max:	100 g/kg

The results appearing in this thesis have been reported as functions of iron dosage expressed as mg Fe/l. The conversion to the unit mmol Fe/l is (based on the molar weight of Fe) is simply 1 mg Fe/l = 0,0179 mmol/l.

4.2 Choice of experimental methods and protocols

As described in the previous chapter the main intent of this study was to investigate the coagulation of dissolved organic substances by a set of different organic cationic polymer coagulants. More specifically, the objective was to study the coagulation itself, if possible disconnected from the influence of subsequent particle separation method, such as depth filtration, sedimentation or flotation. An additional objective was to study relationships between observed coagulation efficiencies and flocculation efficiencies. These objectives constituted important premises with respect to choice of experimental method. Other important premises were, due to strict limitations with respect to time and resources, that the method chosen would have to require minimal time- and cost consumption for assembly and training, and should allow for a large number of experiments to be performed within a short time span.

On the basis of these premises standard jar tests, being a well established and time efficient method, were chosen as the main experimental method. However, the normal particle separation method, settling, was replaced by sequential filtration, directly after flocculation, through filters of decreasing pore diameter (11 μm, 1,2 μm, 0,45 μm) with 0,1 μm membrane filter as the final separation step. The physical set-up of the main experiments is presented schematically in figure 4.1.

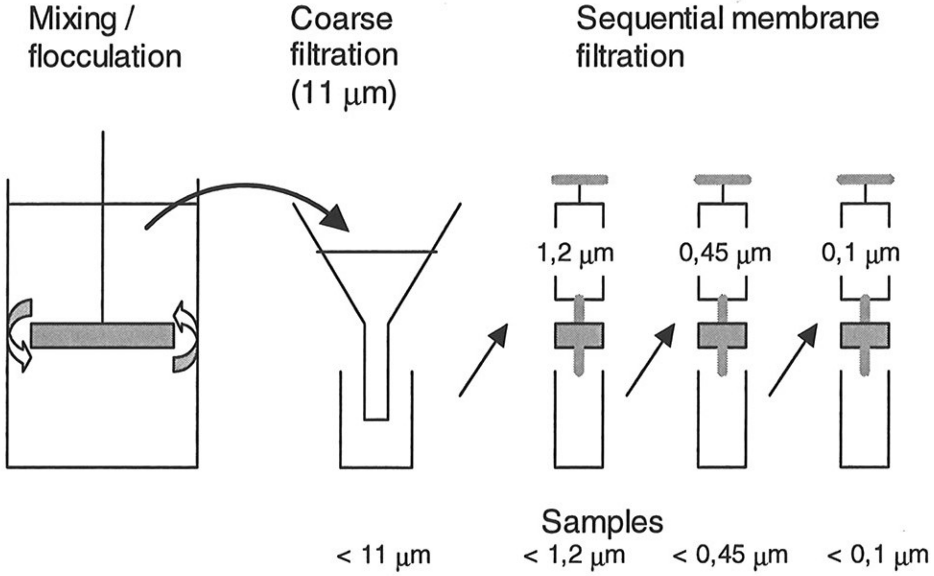


Figure 4.1. Physical set-up of main experiments (schematically)

In principle, this method has also been used by other investigators (Bolto *et al*, 1998; Edzwald *et al*, 1987; Glaser and Edzwald, 1979), the latter showing that the method is well suited to predict optimal doses for cationic polymer coagulants in humic water systems with depth filtration as particle separation method. 0,1 μm membrane filters were chosen as the final filter as an attempt to separate coagulated from non-coagulated matter with the minimal influence from flocculation (size-build up) of the coagulated substances. It is conceivable that coagulation may occur without flocculation to aggregates separable at this pore diameter, but it was considered the best practical approximation to a separation between coagulated and non-coagulated matter. The preceding filters were included partly to give rough size distributions of the organic matter present, partly to prevent clogging of small pore size filters, but mainly in order to monitor the flocculation of the coagulated systems.

With respect to raw waters used in this study, the main focus was intended to be on a practically particle free, humic water. This was achieved by preparing dilutions of a dilution of humic ion-exchange regenerant solution from a waterworks close to Meråker, Norway with tap water. This was chosen mainly because it has been used as the standard humic raw water in extensive studies for a series of years in our group and therefore would provide more comparable results than with the choice of another humic raw water.

For similar reasons, the effluent from a experimental high-rate moving bed bioreactor (MBBR) process was chosen for supplementary experiments on a particle rich raw water with a much more heterogeneous composition of organic substances. This choice was considered to be practical and mutually beneficial relative to a parallel contract project at SINTEF (Melin *et al*, 2002) on combining a high rate MBBR with a coagulation-dissolved air flotation process using organic polyelectrolyte coagulants. The bioreactor obviously alters the composition of the water relative to a raw wastewater, which was considered to be the most likely alternative. However, the compositional variation in municipal wastewaters (site- and time wise) is so large that using the high-rate bioreactor effluent was considered to be as adequate with respect to the purpose of the experiments as random batches of raw wastewater would have been.

4.3 Coagulation experiments with humic water

4.3.1 Experimental design

4.3.1.1 Main framework of experiments

<table>
<tr><td colspan="3">A)
Main experiments

Comparison of coagulation efficiency for chitosan (F_A 0,05), PDADMAC, poly-Epi-amine, low molecular (LMW) and medium molecular weight (MMW) cationic polyacrylamide copolymers (CPAAM) at a standard pH of 6,0</td></tr>
<tr><td colspan="3">B)
Best achievable coagulation using a metal salt coagulant

Establishing optimal pH range and dosage for coagulation of the same raw water with iron chloride sulphate.</td></tr>
<tr><td>C-1)
Effect of pH

on coagulation with selected polyelectrolytes (PDADMAC, chitosans F_A 0,05 and 0,37)</td><td>C-2)
Effect of the degree of acetylation F_A (chitosans)

Effect on coagulation at pH 6 and 4</td><td>C-3)
Effect of the combination of metal salt and polyelectrolytes coagulants

Combined use of low dosage of iron chloride sulphate with low dosage of PDADMAC and chitosan F_A 0,05 at pH 6 and 5</td></tr>
</table>

4.3.1.2 Design of individual experiments

A) Main experiments

The objective of these experiments reflects the main objective of this work: to provide comparative results for the efficiency and performance of different commercially available cationic polyelectrolytes in coagulation of dissolved organic substances in the same humic water. The ambition was to assess the performances over a broad dosage range and with small enough dosage increments to identify possible maxima in dosage responses. Requiring a relatively high number of different dosages for each coagulant, this ambition was considered to be met most practically by using several batches of reproducible constructed humic raw water thereby splitting the total number of dosages to smaller blocks of 6 dosages. In this way experiments with the five different coagulants could be carried out in parallel on the same raw water batches. Furthermore the dosage points in the second block could be chosen partially to complement the dosage points in the first block based on already obtained results and partially to check experimental reproducibility.

For chitosan (F_A 0,05), PDADMAC and MMW CPAAM results from the two planned experimental blocks indicated the need for a third series of experiments in order to check reproducibility with respect to TOC removal, more accurately describe coagulation maxima and if possible obtain an overdosage situation for chitosan and MMW CPAAM.

B) Best achievable coagulation using a metal salt coagulant

The objective of these experiments was to give an indication of maximum obtainable coagulation efficiencies using near optimal dosages of iron chloride sulphate at near optimal coagulation pH for the chosen raw water composition and experimental protocol. Extensive pilot scale three media depth filtration studies previously performed at this institute on basically the same raw water (regenerant solution from the same waterworks diluted with tap water and pH adjusted) had indicated an optimal iron chloride sulphate dose of approximately 7 mg Fe/l at pH 4,5-5,5 (Eikebrokk, 1999, Saltnes, 2002). The jar test experiments were therefore conducted with dosages ranging from 3 to 10 mg Fe/l and pHs ranging from about 4 to about 6,5.

C-1) Effect of pH and C-2) Effect of the degree of acetylation F_A (chitosans)

In order to provide results directly comparable to those obtained at pH 6 (main experiments) these experiments were designed using the same approach as in A). However the ambitions were somewhat lowered, assessing the effect of pH only on coagulation with PDADMAC (a strong polyelectrolyte) and chitosan (a weak polyelectrolyte), and reducing the total number of dosage points for each coagulant to 6. Based on the literature study it was expected that lower dosages were needed at pH for than at pH 6, accordingly the range of the dosage points were shifted downwards based on obtained results at pH 6.

C-3) Effect of the combination of metal salt and polyelectrolyte coagulants

The objective of these experiments was to assess the effect of combining a polyelectrolyte and a metal coagulant at low dosages, but it was not an ambition to describe performances (maxima, over- and under dosages) over a broad range of combinations and dosages. Polyelectrolytes to be tested were restricted to PDADMAC (strong) and chitosan F_A 0,05 (weak), metal salts restricted to only iron chloride sulphate. In order to also assess the effect of pH two coagulation pHs were selected, 6 and 5. pH 6 was chosen to allow for direct comparisons with main experiments, pH 5 was chosen instead of pH 4 as it was considered to be a more realistic coagulation pH in a real-life situation. In order to analyse the results using ANOVA (analysis of variance) a two level full factorial design was adapted for each polyelectrolyte. Instead of performing replicates of corner points three replicates were performed on a centre point.

4.3.2 Preparation and description of raw water

Humic raw water for coagulation experiments was prepared by 1000-fold dilution of anion-exchange regenerant solution from a water treatment plant near Meråker, Norway with tap water from the municipal water treatment plant (VIVA) in Trondheim. The contribution from the dilutant (tap water) was with respect to colour, TOC and turbidity 13 ± 1 mg Pt/l (at pH 8), 2,5 ± 0,3 mg C/l and < 0,25 NTU, respectively. The treatment process at VIVA includes carbonisation (by filtration through calcium carbonate) and pH adjustment, but no coagulation step. A 30-litre batch was prepared for each new day of experiments. Raw water pH was adjusted (normally to pH 6, chosen as a standard condition) with concentrated hydrochloric acid (PA grade).

A sample was drawn from each raw water batch and subjected to the same filtration and analysis protocols as samples of coagulated water. Average raw water composition was as presented in tables 4-3 and 4-4.

Table 4-3. Average composition of unfiltered humic raw water at pH 6,0

Parameter	Average
Alkalinity (mmol/l)	1,0
Calcium (mg Ca/l)	20
Turbidity (NTU)	0,24
Colour (mg Pt/l)	58
Ultra violet absorption (UVA) (m^{-1})	31
Total organic carbon (TOC) (mg C/l)	6,7
Temperature (°C)	14

Table 4-4. Average composition of humic raw water subjected to the same filtration protocol as samples of coagulated water

Parameter	Average for sample aliquot passing			
	11 µm	1,2 µm	0,45 µm	0,1 µm
Turbidity (NTU)	0,19	-	-	-
Colour (mg Pt/l)	58	55	56	54
UVA (m-1)	32	31	32	31
TOC (mg C/l)	6,6	6,7	6,7	6,9
SUVA (l/mg m)	4,9	4,6	4,8	4,5

A somewhat striking feature in table 4-4 is the increase in measured TOC level, especially after the 0,1 µm filtration step. It was suspected that the increase could be caused by leakage of organic matter from the filters themselves. This was checked specifically by submitting distilled water to the same filtration protocol. The results from this investigation did in fact show leakage of organic material (measured as TOC) from the filters. In magnitude the leaked TOC corresponded well with the differences in TOC observed in the different sample aliquots obtained from sequential filtration of the humic raw water. However this was considered to have no or little influence on the results presented in this study as the TOC leaked from filters was assumed to be present in samples of raw water as well as coagulated water (thereby cancelling out the effect on calculated removals).

Eikebrokk (2001) reports a characterisation of the TOC in the same tap water as well as reconstituted humic water (diluted anion exchange regenerate) that was used in this work with respect to molecular weight distribution as measured with HPLC (High Performance Liquid Chromatography). The results showed, as summarized by Saltnes (2002), that the main portion of TOC (68 and 58% in tap water and reconstituted humic water, respectively) was found in the 5 000 – 20 000 Dalton MW-range for tap water as well as for reconstituted humic water. The main contribution of TOC from the humic concentrate (anion exchange regenerant) was in the MW-range 10 000 – 20 000 Dalton.

Fractionations of the humic water with respect to the distribution of TOC on fractions with different charge and degree of hydrophobicity as reported by among others Bolto *et al* (1998) have not been performed. It can be argued however that such a characterisation of the reconstituted humic raw water (diluted anion exchange regenerant), compared to an analogue characterisation of the natural raw water prior to anionic exchange would have been useful considering that the anionic exchange process may well alter the composition of the NOM retrieved from the regenerant solution relative to the composition of NOM found in natural humic waters. It is reasonable to assume that the relative portion of anionic, hydrophobic NOM in the raw water used in this study may have been enhanced in the anion exchange process, and that the reconstituted humic water may therefore be more amenable to coagulation than a natural humic water.

4.3.3 Experimental protocol

Coagulation and flocculation was conducted as jar tests in 1000 ml beakers with a lab scale batch-flocculator (Kemira flocculator model 2000) programmed as follows: 60 seconds rapid mix (started simultaneously with addition of coagulants) at 400 RPM, 20 min slow mixing (flocculation) at 30 RPM.

A step of quiescent settling, as is normally found in jar test protocols, was considered to be superfluous (the objective of the experiments not being to create settleable flocs) and therefore omitted. The effect of omitting the sedimentation step before filtration was however tested and found to be of no or little influence on the final results.

Polyelectrolyte coagulants were added as 1% solutions (except for MMW CPAAM Fennopol K1912 added as 0,1% solution) using an automatic pipette with the tip submerged to deliver the coagulant into the most turbulent zone (directly above and to the side of the stirring paddles).

Directly after the flocculation period, approximately 300 ml of the suspensions were decanted into a gravimetric filtration set up (funnel) holding paper filters with average pore size of 11 µm (Whatman No 1 paper filters). Approximately 100 ml samples of unfiltered coagulated water were collected for pH analysis. After discarding the first 15-20 ml of sample to pass the paper filter approximately 200-250 ml sample was collected in dark glass bottles. After turbidity measurement the samples were stored at 4°C overnight for further filtrations and analysis according to scheme presented below.

Schematic presentation of experimental protocol

Rapid mixing (60 sec/400 RPM) / addition of coagulant
↓
Flocculation (20 min/30 RPM)

↓ decantation to filter → sample aliquot (pH)

Filtration (gravimetric) 11 µm paper (200-250 ml) → sample aliquot
↓

Filtration (syringe) 1,2 µm membrane (50 ml) → sample aliquot
↓

Filtration (syringe) 0,45 µm membrane (20 ml) → sample aliquot
↓

Filtration (syringe) 0,1 µm membrane (15 ml) → sample aliquot

Analysis of pH and turbidity were performed within hours after sample collection, analysis of colour and UVA within 2 days after sample collection. Samples for TOC analysis were acidified with one drop of concentrated phosphoric acid (PA grade) and stored at 4°C until automated analysis could be performed (1 week – 2 months).

Total repeatability and reproducibility of the full experimental and analytical protocol was assessed separately as described in chapter 5.

4.4 Coagulation experiments with wastewater

4.4.1 Experimental design

4.4.1.1 Main framework of experiments

A) Main experiments

Comparison of coagulation efficiency for chitosan (F_A 0,05), PDADMAC, poly-Epi-amine, low molecular (LMW) and medium molecular weight (MMW) cationic polyacrylamide copolymers (CPAAM) at a standard pH of 6,0 using the same experimental protocol as for humic water

B-1) Comparison of jar test protocol with batch flotation protocol

On selected polymers (PDADMAC and MMW CPAAM) alone and in combination with iron chloride sulphate

B-2) Effect of pH

on combined coagulation with PDADMAC and iron chloride sulphate

C) Effect of molecular weight and charge density of CPAAM in batch flotation experiments

CPAAM alone and in combination with iron chloride sulphate

Chitosan alone and in combination with iron chloride sulphate

4.4.1.2 Design of individual experiments

A) Main experiments

Experimental design was based on the same approach as for main experiments on humic water (broad range of dosage points, small increments, testing different coagulants on identical raw water). However not having access to a reproducible raw water (allowing for high number of dosage points for each coagulant on identical raw water) ambition levels had to be adjusted with respect total number of dosage points for each coagulant (reducing this to 6), giving priority to testing of all coagulants (that had been used in main experiments on humic water) on the same raw water. The design with 6 different dosages of each coagulant was conducted with two different raw water batches (08.11.01 and 05.12.01).

In the last experiment series a selection of experimental points were submitted to settling as particle separation method in parallel to the standard sequential filtration protocol.

B-1) Comparison of jar test protocol with batch flotation protocol

In order to compare results obtained in the standard jar test/filtration protocol with results obtained using a more realistic method of particle separation a set of coagulation experiments were performed in parallel with batch dissolved air flotation experiments on the same raw water batches. The design included combinations of constant dosages (2 mg/l) of PDADMAC with 4 dosage levels of iron chloride sulphate (0 , 0,1 , 0,2 and 0,3 mmol Fe/l) and constant dosages (2 mg/l) of MMW CPAAM with 2 dosage levels of iron chloride sulphate (0 and 0,2 mmol Fe/l). The lab -scale batch flotation experiments were part of a contract project at SINTEF (Melin *et al*, 2002).

B-2) Effect of pH

Effect of pH on combined coagulation with PDADMAC and iron chloride sulphate was assessed in two sets of experiments supplementing design B-1 above. pH of raw water was adjusted with concentrated hydrochloric acid prior to coagulation to give coagulation pHs of approximately 7 and 5,5. Coagulation experiments on pH adjusted raw water were restricted to combinations of 2 mg/l PDADMAC with 0,1 mmol Fe/l.

C) Effect of molecular weight and charge density of CPAAM in batch dissolved air flotation experiments

The use of dissolved air flotation as particle separation method (instead of initial filtration through 11 µm paper filter) had two reasons. First it was desirable to include some experiments with a more realistic particle separation method in the study, second it was desirable that the results obtained would be directly comparable to the results obtained in the contract project at SINTEF (Melin *et al*, 2002), through which the specific polyelectrolyte test set to be tested was provided. For the same reasons it was chosen to perform the experiments at ambient raw water pH (around 8,0) rather than at a pH adjusted to 6,0. However sample aliquots were taken through the same sequential filtrations (except through 11 um) as in the previously described experiments.

The experiments to test independent effects of polyelectrolyte charge density and molecular weight using the MMW CPAAM test set provided by Kemira (described in chapter 4.1, table 4-2) were set up as two separate Box Benkhen-designs, one with the polyelectrolytes as sole coagulants, one in which they were combined with the dosage of 0,2 mmol/l Fe^{3+} as iron chloride sulphate. Each design included three levels of charge density (3,0 – 3,5 –4,0 meq/g), three levels of MW (4 – 5 – 6 mill Daltons) and three levels of polyelectrolyte dosage (1 – 2 – 3 mg/l and 2 – 4 – 6 mg/l respectively for the design including and excluding iron chloride sulphate as a co-coagulant). Each point in the designs was performed once, except the centre points (3,5 meq/g – 5 mill – Dalton – 2 / 4 mg polyelectrolyte/l respectively), which were replicated four times to provide estimates of experimental uncertainty for the data analysis.
The actual designs and set-up of experiments were generated using statistical software (The Unscrambler v. 7.5, Camo). Because of the extent of the designs only one could be performed per day (or raw water batch) and it was chosen to perform each separate design (with and without iron chloride sulphate) on two separate days (23.01.02 and 30.01.02).

In addition the two chitosans (F_A 0,05 and F_A 0,37) were tested with the same dosage points, but outside of the Box Benkhen-designs, with and without iron chloride sulphate.

4.4.2 Description of raw water

Coagulation experiments on wastewater were performed on effluent water from a highly loaded lab scale moving bed biofilmreactor (MBBR) fed with municipal wastewater from a nearby residential area. The MBBR was operated at very high loading rate (15 min detention time) as part a contract project at SINTEF (Melin *et al*, 2002) investigating a treatment process for wastewater.

The process combines a biofilm process with coagulation and dissolved air flotation using combinations of metal salt and polyelectrolyte coagulants and is presented schematically in figure 4.2.

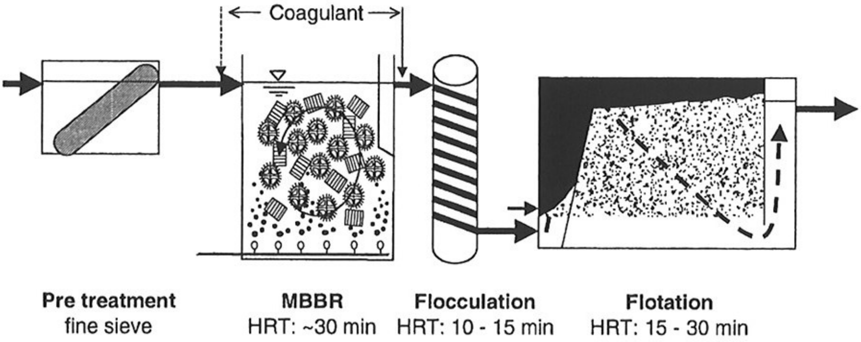


Figure 4.2. Schematic of combined moving bed biofilm and coagulation-dissolved air flotation process for treatment of wastewater (from Melin *et al*, 2002). Raw water for coagulation experiments on wastewater reported in this thesis were taken from the outlet of the MBBR in periods with no coagulant dosage to the inlet of the MBBR.

4.4.2.1 Raw waters used in jar tests 08.11.01 and 05.12.01

Coagulation experiments were performed on two occasions with raw water (35 litre) collected from the bioreactor outlet the same day. To maintain a homogeneous solution (prevent settling of particles) the raw water batch was kept under constant stirring. Raw water pH was adjusted to pH 6,0 with concentrated hydrochloric acid.

A sample was drawn from each raw water batch and subjected to the same filtration and analysis protocols as samples of coagulated water. Raw water composition was as presented in tables 4-5 and 4-6.

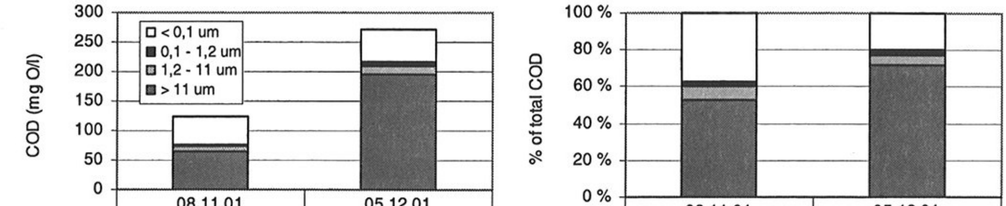
Table 4-5. Composition of unfiltered biofilmreactor effluent (used as raw water in coagulation experiments).

Parameter	08.11.01	05.12.01
pH (adjusted)	6,0	6,0
Turbidity (NTU)	43	91
Suspended solids (mg/l)	-	180
COD (mg O/l)	123	272

Table 4-6. Composition of biofilmreactor effluent subjected to the same filtration protocol as samples of coagulated water

Parameter	08.11.01 sample aliquot passing			05.12.01 sample aliquot passing		
	11 μm	1,2 μm	0,1 μm	11 μm	1,2 μm	0,1 μm
Turbidity (NTU)	5,5	-	-	6,6	-	-
COD (mg O/l)	58	49	46	76	62	55
UVA (m-1)	-	-	36	-	-	38
TOC (mg C/l)	-	-	17	-	-	21

A graphical presentation of the size distribution of the organic matter (COD) in the raw water batches is given in figure 4.3 below.



	08.11.01	05.12.01
□ < 0,1 um	46	55
■ 0,1 - 1,2 um	3	7
▨ 1,2 - 11 um	9	14
▩ > 11 um	65	196

	08.11.01	05.12.01
□ < 0,1 um	37 %	20 %
■ 0,1 - 1,2 um	3 %	3 %
▨ 1,2 - 11 um	7 %	5 %
▩ > 11 um	53 %	72 %

Figure 4.3. Absolute and relative size distribution of organic matter in biofilmreactor effluent (used as raw water in coagulation experiments) measured as COD in sample aliqouts passing 11 µm, 1,2 µm and 0,1 µm filters.

Figure 4.3 shows that the total concentration of organic matter is approximately twice as high in the raw water used in the experiments performed on 05.12.01 than those performed on 08.11.01. This is probably due to higher dilution by drainage water in the latter. The higher content of organic matter in 05.12.01 is mainly made up by particles in the size range above 11 µm. With respect to dissolved organic matter (< 0,1 µm) measured as COD, the concentrations in the two raw water batches are comparable, but the relative portion of dissolved organic substances is twice as high in raw water 08.11.01 than 05.12.01.

4.4.2.2 Raw water used in jar tests combining organic and inorganic coagulants

Coagulation experiments were performed on raw water (35 litre) collected from the bioreactor outlet the same day. In order to compare results with results from dissolved air flotation experiments (Melin *et al*, 2002) on the same raw water and with identical coagulants and dosages the bioreactor outlet stream was split in two while collecting raw water, providing two near identical batches. To maintain a homogeneous solution (prevent settling of particles) the raw water batch was kept under constant stirring. Experiments were performed at ambient raw water pH and at pHs lowered by addition of concentrated hydrochloric acid.

A sample was drawn from the raw water batch and subjected to the same filtration and analysis protocols as samples of coagulated water. Raw water composition was as presented in tables 4-7 and 4-8.

Table 4-7. Composition of unfiltered biofilmreactor effluent (used as raw water in coagulation experiments)

Parameter	21.11.01
pH	8,2
Turbidity (NTU)	28
Suspended solids (mg/l)	120
COD (mg O/l)	175

Table 4-8. Composition of biofilmreactor effluent subjected to the same filtration protocol as samples of coagulated water

Parameter	21.11.01 sample aliquot passing		
	11 µm	1,2 µm	0,1 µm
Turbidity (NTU)	4,5		
COD (mg O/l)	85	50	44
UVA (m-1)			40

4.4.2.3 Raw waters used in batch dissolved air flotation experiments (23.01.02 and 30.01.02)

Coagulation experiments were performed on two occasions with raw water (35 litre) collected from the bioreactor outlet the same day. To maintain a homogeneous solution (prevent settling of particles) the raw water batch was kept under constant stirring. Raw water pH was adjusted to pH 6,0 with concentrated hydrochloric acid.

A sample was drawn from each raw water batch and subjected to the same filtration and analysis protocols as samples of coagulated water. Average raw water composition was as presented in tables 4-9 and 4-10.

Table 4-9. Composition of unfiltered biofilmreactor effluent used as raw water in batch dissolved air flotation experiments

Parameter	23.01.02	30.01.02
pH	8,1	8,0
Suspended solids (mg/l)	90	95
COD (mg O/l)	208	216

Table 4-10. Composition of biofilmreactor effluent used as raw water in batch dissolved air flotation experiments subjected to standard sequential filtration protocol

Parameter	23.01.02 sample aliquot passing			30.01.02 sample aliquot passing		
	11 μm	1,2 μm	0,1 μm	11 μm	1,2 μm	0,1 μm
COD (mg O/l)	122	82	54	128	82	52
UVA (m-1)	-	-	34	-	-	37

4.4.3 Experimental protocol – jar tests

In order to allow for comparisons with coagulation of dissolved organic matter in humic water the same general experimental protocol as used for humic raw water and described in chapter 4.2.2 was adapted for wastewater experiments. However samples were not filtered through 0,45 μm membrane filters and analysis of colour was replaced with analysis of chemical oxygen demand COD. The effect of omitting the sedimentation step prior to gravimetric filtration was not assessed for coagulation of wastewater.

In the experiments performed 05.02.01 jars were, subsequent to decantation of approximately 200 ml for filtration, submitted to 20 minutes of quiescent settling. Based on visual inspection, samples (100 ml) of supernatant were drawn after sedimentation from jars exhibiting the best particle removal by settling (3 jars per series of 6 for each coagulant tested). The samples were analysed for turbidity, suspended solids and COD.

4.4.4 Experimental protocol - batch dissolved air flotation

Batch dissolved air flotation experiments on wastewater were performed according to a protocol developed for a contracted project at SINTEF (Melin *et al*, 2002) using an Aztec flotation jar tester (Severn Trent Services, Capitol controls Ltd, England). Coagulants were dosed with syringes under rapid mixing (400 rpm) which was continued for 60 sec. In experiments with combined use of polyelectrolyte and iron chloride sulphate these were dosed simultaneously. The water was then flocculated for 20 min while mixing at 80 rpm. In the flotation step, 150 ml (15% recycle rate) of distilled water saturated with air under 5 bar pressure was used as dispersion water. The dilution effect of dispersion water was taken into account when calculating the results. The samples were taken 10 min after dispersion water was added. Sample aliquots were taken for sequential filtration through 1,2 and 0,1 µm membrane filtration.

4.5 Analytical methods

pH was measured using a Radiometer ION 83 ion meter fitted with a Radiometer pHC 2701-7 combined pH electrode

Alkalinity was measured on a Metrohm 726 Titroprocessor fitted with a Metrohm 6.0232.100 pH electrode.

Turbidity was measured with a HACH 2100N turbidity meter in the Ratio mode.

Calcium was measured with ICP-MS (external laboratory).

Colour and UV-absorption (UVA) was measured on a Hitachi U-3000 spectrophotometer.

Colour was measured according to Norwegian Standard method for water examination NS 4787 using a 50 mm glass cuvette. Absorption at 410 nm was recalculated to colour units (mg Pt/l) based on a K_2PtCl_6 calibration curve.

UVA was measured as absorption at 252 nm using a 10 mm quartz cuvette.

Total organic carbon TOC was measured on a Tekmar Dohrmann Apollo 9000 combustion analyser calibrated for a 0-20 mg C/l concentration range. Wastewater samples were submitted to 5-fold dilution prior to analysis.

Suspended solids was measured according to Norwegian Standard method for water examination NS 4764 using 1 µm Whatman GF/C filters and filtration volumes around 50 ml.

Chemical oxygen demand was measured with the dichromate method according to Dr Lange method LCK 315 (15-150 mg O/l) using a Dr Lange Lasa 20 photometer.

Analytical repeatability on samples relevant to this study (raw and coagulated humic water and wastewater) was checked for pH, turbidity, colour, UVA, TOC and COD as reported in appendix B.

4.6 Uncertainty of results

4.6.1 Quantitative estimates of uncertainty in results from coagulation experiments on humic water

The uncertainty of the results from coagulation of humic water has been investigated in terms of total experimental repeatability as well as reproducibility. Tests of experimental repeatability were used to provide quantitative measures for single data point uncertainties, whereas reproducibility was assessed qualitatively. In addition the repeatabilities of the analytical methods have been estimated.

Repeatability of the results from the coagulation experiments on humic water was investigated by performing six full parallels of a coagulation experiment with a dosage of 10 mg/l chitosan to standard humic raw water. This dosage resulted in removals of approximately 80%, 50% and 25% of colour, UVA and TOC respectively, thus providing an estimate of total experimental repeatability at near optimal conditions (with respect to maximal removals). It is assumed that this estimate is valid also for coagulation at near optimal conditions with the other cationic polyelectrolytes used in this study. The estimate is not necessarily valid at sub-optimal dosages. This is however not considered to be a problem as the quantitative interpretation of the results has been restricted to the near optimal region, whereas the interpretation of results in the sub-optimal region have been of a more qualitative nature.

Total experimental repeatability expressed as the standard deviation of the results for each analytical parameter differed for the different filtration steps (11, 1,2, 0,45 and 0,1 µm). However, the differences were not statistically significant at the 95% probability level. Therefore it was decided to use one average measure of uncertainty for each analytical parameter, regardless of filtration step sample aliquot. The average of the confidence intervals at 95% probability, n=1 repetitions, (calculated from the standard deviations) for each filtration step was chosen as an uncertainty measure for individual data points, and are reported together with average relative standard deviations in table 4-11 below.

As most of the results are reported as % relative removals the corresponding uncertainty measure for this quantity has been provided by calculating removals for each repetition relative to filtrations and analysis of six parallel samples from the same raw water batch. This was done in order to incorporate the uncertainty of raw water filtration and analysis in the total uncertainty measure for the relative removals.

Table 4-11. Relative standard deviations and total experimental uncertainty measures for coagulation experiments on humic water using cationic polyelectrolytes. Based on 6 full parallels of coagulation experiment using 10 mg/l of chitosan.

Statistical parameter	Analytical parameter				
	Turbidity	Colour	UVA	TOC	pH
Relative standard deviation for absolute result	6 %	3 %	2 %	5 %	
Total experimental uncertainty for individual data points, absolute results (confidence interval at 95%, n=1)	0,06 NTU	0,6 mg Pt/l	0,4 m^{-1}	0,5 mg C/l	0,1
Relative standard deviation for relative removal result		0,8 %	2 %	16 %	
Total experimental uncertainty of individual results reported as % relative (confidence interval at 95%, n=1)		1 %	2 %	8 %	

4.6.2 Evaluation of reproducibility of coagulation experiments on humic water

Reproducibility of the coagulation experiments on humic water has been qualitatively assessed by plotting results from experiments performed at different times with different raw water batches in the same graphs. The graphs were then investigated visually in order to determine whether or not the results could have originated from one single experiment. This method does not provide a quantitative measure on the experimental reproducibility, but was considered to offer proof of reproducibility sufficient for this study.

Examples (from coagulation of humic water with chitosan at pH 6) of the kind of graphs used for this purpose are given below.

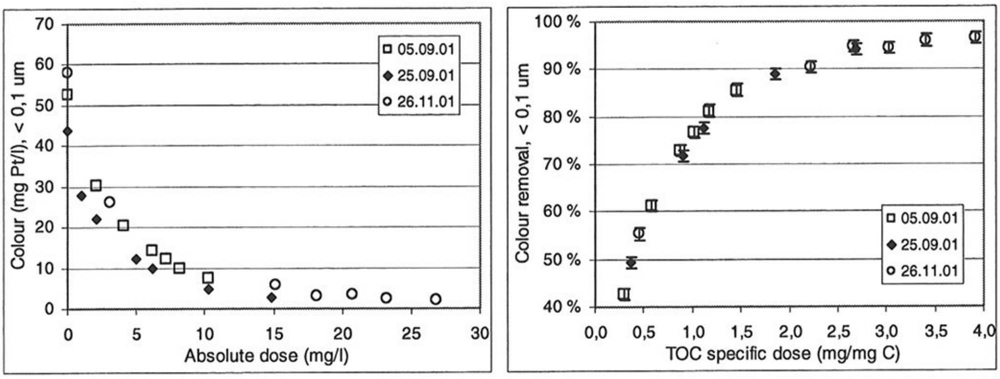


Figure 4.4. Reproducibility in coagulation experiments with chitosan on different batches of humic water. Colour (residual and relative removal) after coagulation, flocculation and final filtration through 0,1 μm pore size membrane filter. The legends denominate the date on which the experiments were performed.

Plot of residual colour as function of chitosan dose after coagulation, flocculation and final filtration through 0,1 μm (figure 4.4 left) shows that reproducibility was not achieved with respect to raw water concentrations (here reported as colour) and that the same absolute dose of chitosan gave different values of residual colour for different raw water batches. This is in accordance with the dose-removal stoichiometry generally found for coagulation of humic waters with polyelectrolytes.

In order to be able to collectively investigate results from different coagulation experiments it was necessary to plot the results as relative removals as function of TOC specific dose (dose as mg/l divided by TOC as mg C/l in unfiltered raw water), as shown in figure 4.4, right part. Visual inspection of this graph shows that the data points could just as well have originated from one single experiment, thus providing qualitative evidence of acceptable experimental reproducibility with respect to colour removal. Reproducibility in experiments with the other cationic polyelectrolytes tested in this study, as well as removals after filtration steps 11, 1,2 and 0,45 μm, was investigated in the same way and showed in general the same acceptability. This was also true with respect to UVA-removal.

With respect to TOC removal a somewhat poorer reproducibility was observed as can be seen in different plots of relative removal of TOC as functions of

TOC specific dose. However the total experimental uncertainty as estimated from repeatability tests was also found to be significantly higher for TOC removal results. It was therefore decided to accept a poorer reproducibility for TOC removal results without further investigations.

4.6.3 *Quantitative estimates of uncertainty in results from coagulation experiments on biofilmreactor effluent*

In the experiments on biofilm reactor effluent estimates of uncertainty in analysis results (appendix B, table B) have been used to estimate the uncertainty of individual data points.

4.7 General presentation and interpretation of results

More than 95 % of NOM (measured as colour, UVA or TOC) in the humic water used in this study is present in a dissolved state. Dissolved is here defined operationally as passing though a 0,1 μm membrane filter. It has not been an objective in this study to investigate whether the substances are truly dissolved in a thermodynamic understanding of the word or stable colloidal matter. Consequently no attempt has been made to specifically determine whether aggregates are formed as result of a coagulation process (assuming NOM is in the particulate form) or a precipitation process (assuming NOM is in the truly dissolved state). For simplicity the term coagulation, being the most commonly used term in studies on the interaction between NOM and polyelectrolyte coagulants, has been used in this study regardless whether or not the actual aggregate forming process is coagulation or precipitation.

Coagulation has in this study been defined operationally (analogue to the operational definition of dissolved) as the formation of aggregates that are withheld in a 0,1 μm membrane filter. Quantitatively, coagulation has been defined and measured as the removal of dissolved matter from the raw water:

$$\text{Coagulated matter} = \text{Dissolved matter in raw water sample} - \text{Dissolved matter in sample of coagulated water}$$

The correctness of this definition can be discussed, especially at high polymer dosages, as it is well conceivable that formation of particulate NOM-coagulant aggregates with sizes under 0,1 μm (without flocculation to larger particles) may occur. It is however in good accordance with the general understanding of the term in our field of science and has been considered practical for this study.

The experimental protocol has, as described in chapter 4, included filtration of all samples through 11 μm paper filter directly after flocculation followed by filtration through 1,2 μm, 0,45 μm and 0,1 μm membrane filters in sequence and with collection of sample aliquots after each filtration. With a few exceptions all sample aliquots have been analysed with respect to colour, UVA and TOC. By comparing results after filtration through 0,1 μm membrane filters (assumed to reflect the systems coagulation state) with results after filtration through filters with larger pore sizes (cutting off larger flocs) it is possible to evaluate also the floc forming properties of the aggregates formed by coagulation.

Interpretations of flocculation results have been restricted to qualitative evaluations of a given systems ability to produce flocs withheld by the various pore sizes relative to the degree of coagulation (amount of aggregates formed) in the system. A system reaching a high degree of coagulation as measured by removals after filtration through 0,1 μm, but failing to reach a high degree of flocculation as measured by cut off by larger pore sizes is in this manner understood to produce aggregates with poor flocculation properties.

In general the results from the different coagulation experiments have been reported graphically in plots of relative removals as function of TOC specific dose (dose as mg polyelectrolytes/l divided by mg C/l TOC in unfiltered raw water). For each polymer two types of removal plots have been made as exemplified below for PDADMAC; one type showing removals after filtration through different filter pore sizes for each analytical parameter in one plot (single polymer-multiple fractions) and one type compiling removals for different analytical parameters (colour, UVA and TOC) after each final filtration step in one plot.

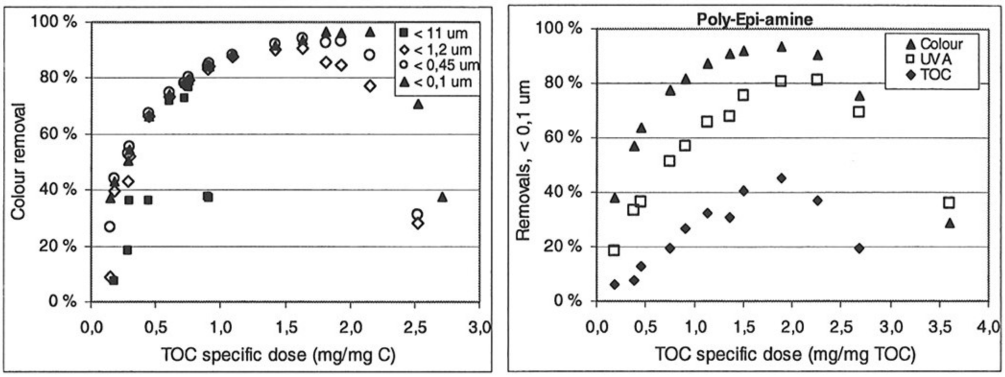


Figure 4.5. Left: Relative removal of colour from humic water as function of TOC specific polymer dose (mg/l polymer added divided by mg Pt/l in raw water) after coagulation with PDADMAC C-591 and serial filtration through filters with pore sizes 11, 1,2, 0,45 and 0,1 μm. The legend denominates the filter pore sizes through which the sample aliquots have passed before measurement (including raw water). **Right:** Comparison of relative removals of UV-absorbing substances (UVA, m^{-1}), total organic carbon (TOC, mg C/l) and colour (mg Pt/l) from humic water as function of TOC specific polymer after coagulation with poly-Epi-amine C-581 and filtration through Whatman no 1 paper filter (pore size 11μm).

As the main focus of this study has been to compare the performance of different cationic polyelectrolytes coagulants, selected plots of this kind (single polymer) have been taken into the main text only when needed to illustrate certain phenomena of special interest.

Direct comparisons of the performance of different polymers are generally presented as plots of removals observed for different polymers for one analytical parameter and after one final filtration step, as exemplified below.

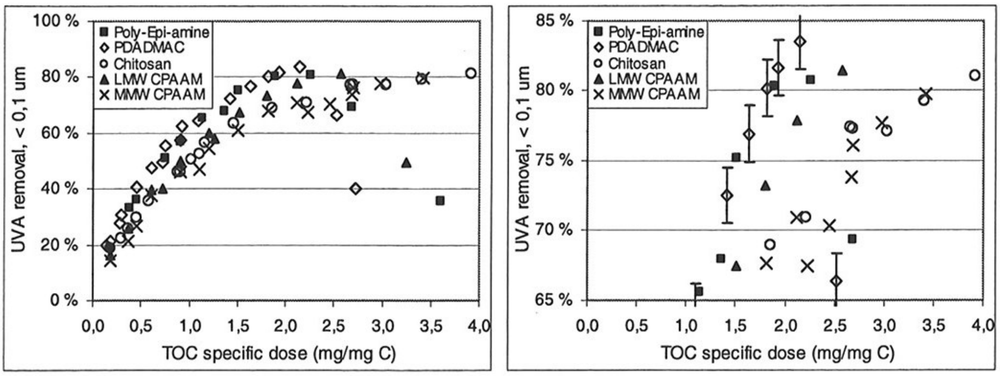


Figure 4.6. Left: Relative removal of UV-absorbing substances from humic water as function of colour specific polymer dose (mg/l polymer added divided by mg C/l TOC in raw water) after coagulation and final filtration through 0,1 μm pore size membrane filter. Comparison of removal efficiencies of different cationic polymers. **Right:** Enlargement of selected region including error bars representing single data point uncertainty.

Again, only selected plots are presented in the main text to show specific findings. Interpretation of the results is mainly based on findings from visual inspections of these graphical presentations.

4.7.1 Definition of terms used to describe polymer performance

Coagulation efficiency	Relative removal (%) of dissolved substances (passing a 0,1 μm membrane filter)
Polymer dose efficiency	Relative removal (%) per mg/l polymer added
Cationic charge dose	Dose of cationic charge equivalents (μeq/l) provided by dosage of cationic polyelectrolytes. Defined as polymer dose in mg/l multiplied by polymer cationic charge density in μeq/mg.

Cationic charge dose efficiency	Relative removal (%) per μeq/l cationic charge added in form of polyelectrolyte
TOC-specific dose	Polymer dose (or cationic charge dose) per mg TOC in raw water
TOC-specific dose efficency	Relative removal (%) TOC-specific polymer (or cationic charge) dose

5 RESULTS AND DISCUSSION ON COAGULATION AND FLOCCULATION OF NOM IN HUMIC WATERS

The main objective of this work has been to determine how organic cationic polymers can coagulate dissolved organic substances in water.

This was broken down into the following specific sub objectives:

- By choice of experimental methodology, to study the coagulation process (of dissolved organic substances) as such, disconnecting the obtained results from dependency on floc growth and separability of formed flocs
- To compare coagulation efficiency and performance of a wide spectre of different cationic polyelectrolyte coagulants, over a broad dosage range (regardless of economical concerns), ranging from sub optimal dose to overdosage (if obtainable)
- To offer a comparison of maximal achievable coagulation, with the selected experimental method, using cationic polyelectrolyte coagulants relative to using a known effective metal salt coagulant under optimal conditions
- To compare the dosage response with respect to coagulation relative to flocculation of the formed aggregates
- To compare coagulation dosage response of coloured and UV-absorbing NOM relative to the bulk of the NOM (measured as TOC)

The main objective in the choice of polymers for testing was to cover a wide spectrum of different cationic polyelectrolyte coagulants, with emphasis on "cationic" and "coagulant", covering a broad variation in chemical structure and charge density within the range of commonly used and commercially available product types. It was of special interest to investigate the effect of polyelectrolyte chemical composition and charge density relative to the effect of the mere addition of cationic charge equivalents. Furthermore it was of special interest to examine the performance of chitosan (being a non-toxic biopolymer) relative to synthetic polymers. Thorough testing of the effect of polymer molecular weight on coagulation of dissolved organic matter was not a principal ambition and was reflected in the choice of polymers. However, as there appears to exist some controversy on this issue in the literature (chapter 2.5.4), it was decided to include a medium molecular cationic polyacrylamide

(CPAAM) for testing against a low molecular weight CPAAM with approximately the same charge density.

In order to further specify the main issues to be investigated a set of hypotheses were formulated and are stated in sub chapter 3.1.

5.1 Coagulation and flocculation of NOM at pH 6,0

5.1.1 Results from the main experiments in overview

As lined out in chapter 4 the experiments on humic water have been divided into a set of so called main experiments and a set of supplementary experiments. The main experiments consist of experiments performed to describe and compare the coagulation and flocculation performance of all the different polyelectrolyte types in reproduced batches of raw water at pH 6. This subchapter is included in order to give a brief overview of the results and point out the most important findings presented in sub chapter 5.1.

An overview of the results from the main experiments are presented below in figure 5.1 as the coagulation and flocculation of coloured substances as well as residual turbidity after filtration through 11 μm paper filter.

The following main features can be identified in figure 5.1 (below):

- The upper left part of figure 5.1 shows that all polyelectrolytes tested are efficient coagulants for NOM and appear to reach approximately the same level of removal, although at different dosages. Elaborate discussions of the performance of the different polyelectrolytes and comparison with coagulation results obtained with iron chloride sulphate are given in sub chapter 5.1.3.
- There appears to exist a distinct difference between dose efficiency for PDADMAC and poly-Epi-amine on one hand and chitosan and CPAAMs on the other (upper left part of figure 5.1). In sub chapter 5.1.4 it will be shown that the difference in dose efficiency with respect to coagulation is an effect of the difference in charge densities. It will also be shown that the nature of the effect of charge density is predominantly related to different additions of charge equivalents and not to differences in spatial distribution of charge.

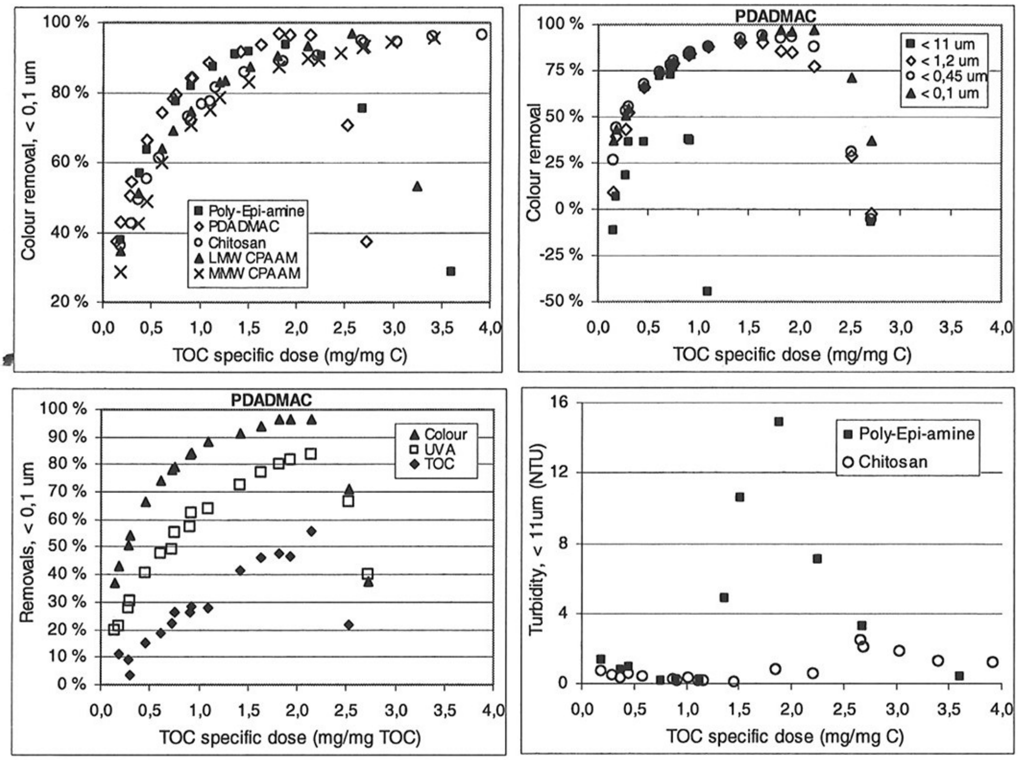


Figure 5.1. Results from main experiments in overview.**Top left:** Comparison of coagulation performance (measured as removal of coloured substances) for the different polyelectrolytes. **Bottom left:** Relationship between coagulation of coloured substances, UV-absorbing substances (UVA) and total organic carbon exemplified by PDADMAC. **Top right:** Comparison of dosage response with respect to coagulation and the ability of the formed agregates to flocculate exemplified by PDADMAC. **Bottom right:** Difference between chitosan and synthetic polyelectrolytes (exemplidied by poly-Epi-amine) with respect to aggregate flocculation properties expressed as residual turbidity after coarse filtration (11 μm)

- The bottom left part of figure 5.1 shows (exemplified with PDADMAC) that apart from a relatively parallel displacement with respect to removal levels, the dosage responses with respect to coloured, UV-absorbing and bulk NOM (measured as TOC) are very similar. This will be investigated in further detail in sub chapter 5.1.3.
- The upper right part of figure 5.1 shows (exemplified with PDADMAC) that coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes and that the polyelectrolyte dosage providing maximal

coagulation of dissolved organic substances is not identical to the dosage providing aggregates with the best flocculation properties.

- The bottom right part of figure 5.1 shows a distinct difference between chitosan and the synthetic polyelectrolytes (exemplified by poly-Epi-amine) with respect to residual turbidity after coarse filtration, especially at high dosages. In sub chapter 5.1.3 it will be argued that this probably is an indication of that chitosan forms aggregates that flocculate more readily than aggregates formed by the synthetic polyelectrolytes.

5.1.2 Coagulation with iron chloride sulphate as sole coagulant

The objective of the experiments using iron chloride sulphate as sole coagulant has been to provide a reference for comparison with coagulation experiments using cationic organic polymers, alone and in combination with low dosages of iron chloride sulphate. More specifically the experiments were aimed at finding the optimal coagulation conditions with respect to dosage and pH for the given raw water type using iron chloride sulphate as coagulant and using the same experimental protocol as for experiments with organic polymer. Furthermore to establish what coagulation efficiencies measured as removal of colour and TOC after final filtration through 0,1 μm membrane filter could be achieved using iron chloride sulphate.

The experiments with iron chloride sulphate were performed at to different occasions, partly to establish reproducibility and partly to provide supplementary experimental points (dosage and pH). The results are presented as removal of colour and TOC after final filtration through 0,1 μm membrane filter as function of dosage (mg Fe/l) and coagulation pH in figure 5.2 below.

Figure 5.2 shows that for the current raw water and experimental protocol optimal iron chloride dosage with respect to coagulation of NOM was 7 mg Fe/l. Optimum pH appears to range from approximately 4,5 to 5,5.

The highest observed coagulation efficiency measured as removal after final filtration through 0,1 μm membrane filter is close to 100% with respect to colour and about 70% with respect to TOC.

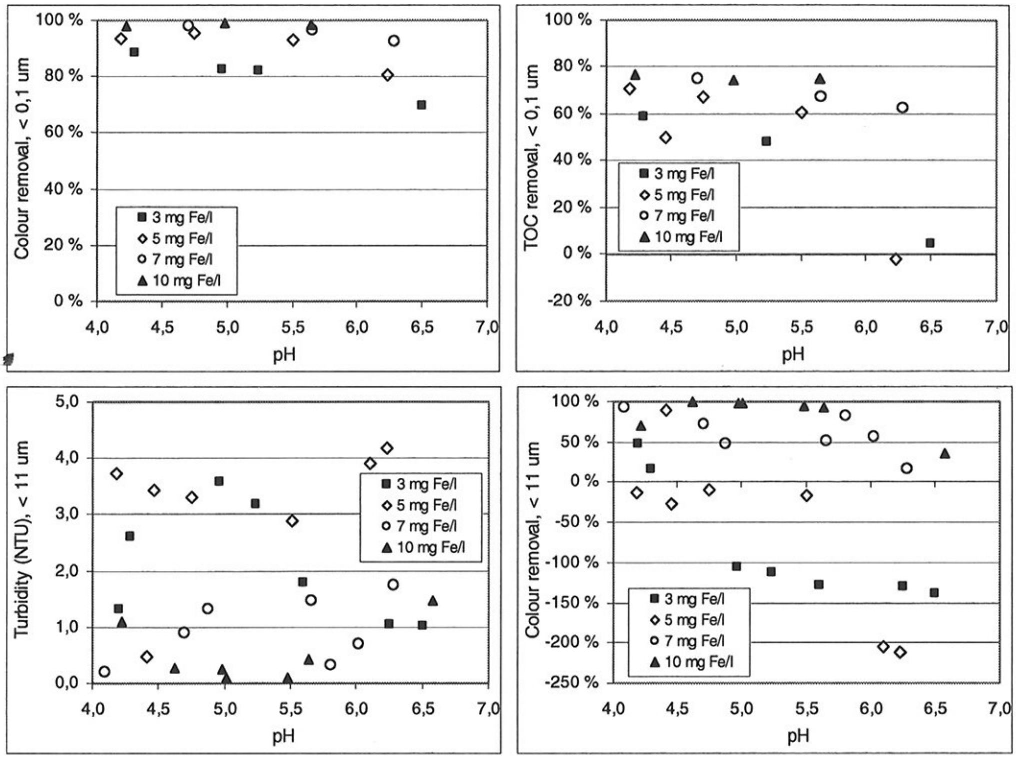


Figure 5.2. Top: Coagulation of NOM with iron chloride sulphate measured as removal of colour and TOC after final filtration through 0,1 μm membrane filter as function of dosage (mg Fe/l) and coagulation pH. **Bottom left:** Residual turbidity after filtration through 11 μm paper filter as function of dosage (mg Fe/l) and coagulation pH. **Bottom right:** Flocculation properties of aggregates measured as removal of colour after final filtration 11 μm paper filter function of dosage (mg Fe/l) and coagulation pH.

The bottom graphs in figure 5.2 to illustrate how flocculation is influenced by iron chloride dosage and coagulation pH. Although dosages as low as 3 mg Fe/l are sufficient to achieve acceptable coagulation (80 %) flocculation measured as removal of colour and residual turbidity after filtration through 11 μm paper filter is poor at this low dosage. Dosages of 7 to 10 mg Fe/l are necessary to obtain a high degree of coagulation as well as good flocculation of aggregates. It is natural to assume that this fact must be attributed to the importance of iron hydroxide precipitates both as adsorbents for NOM and by increasing the total particle concentration, and thereby the flocculation speed, in the system.

5.1.3 Formation and flocculation of NOM-polymer aggregates

5.1.3.1 Comparison of coagulation dosage responses of the different polyelectrolytes

Coagulation has in this study been defined operationally (subchapter 4.7) as the formation of aggregates that are withheld in a 0,1 μm membrane filter. Quantitatively, coagulation has been defined and measured as the removal of dissolved matter from the raw water:

Coagulated matter = Dissolved matter in raw water sample
- Dissolved matter in sample of coagulated water

Accordingly coagulation has been monitored as the relative removal of colour, UV-absorbing substances (UVA) and TOC after final filtration through 0,1 μm.

Coagulation of NOM at pH 6,0 with the different polymers tested is presented as removal of colour, UVA (UV absorbency) and TOC as function of TOC-specific polymer dose (mg polymer/mg TOC) in figure 5.3 below. Removal of colour after filtration through 11 μm paper filter has been included in figure 5.3 since flocculation properties of the aggregates formed in the coagulation process also have to be considered with respect to optimal dosages in a practical perspective.

Figure 5.3 (upper and lower left parts) show that all polyelectrolytes tested are efficient in coagulating coloured and UVA substances. Furthermore, all polyelectrolytes appear to reach approximately the same maximum levels of removal with respect to colour and UVA, but different dosages are required.

Removals up to 95% of colour and 80 % of UVA are observed, but relatively high dosages are required, 1,5 to 3,0 mg/mg TOC depending on polymer type, to reach these maximum levels of removal. For the humic water used in this study (average colour, UVA and TOC of respectively 54 mg Pt/l, 31 m^{-1} and 6,6 mg C/l) these TOC specific dosages correspond to 10 to 20 mg/l. Removals of TOC are generally lower and reaching maximums of 45-50%.

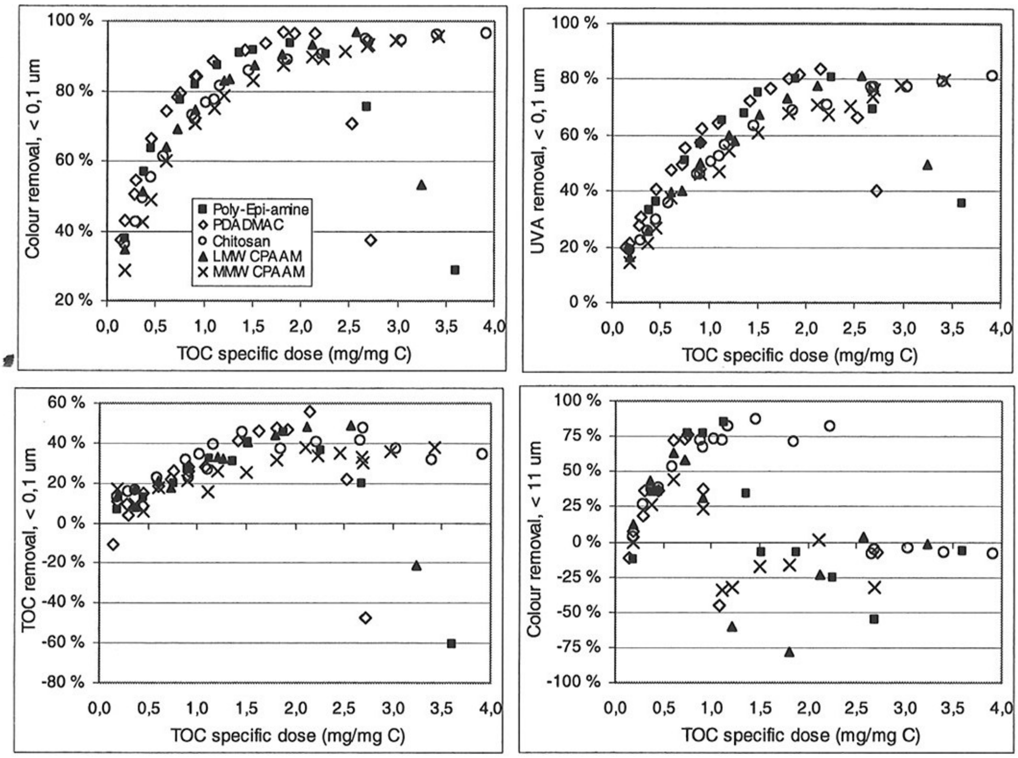


Figure 5.3. Comparison of NOM-coagulant aggregate formation in humic water by cationic polyelectrolytes monitored as removal of NOM (measured as colour, UVA and TOC) after final filtration through 0,1 μm membrane filter. Bottom right: Removal of colour after filtration through 11 μm paper filter.

The relationship between coagulation of NOM and the flocculation properties of the formed aggregates will be investigated in more detail in the next sub chapter. However, it is of practical relevance to notice right away that the high dosage levels required achieving the highest observed levels of coagulation result, for all polyelectrolytes except for chitosan, in aggregates with sub optimal flocculation properties. This is seen clearly when comparing the upper left and lower right parts of figure 5.3. The high dosage levels (10 to 20 mg/l) required to achieve maximum coagulation would in most real-life situations be considered to be practically and economically unrealistic. However, the optimal dosage levels for removal after filtration through 11 μm (0,5 to 1,0 mg/mg TOC) are far more realistic from a practical point of view and will still give coagulation efficiencies in the range of 65 to 80%. In many cases a removal level in this range would be sufficient to achieve an acceptable water quality with respect to colour.

This is illustrated best by an example:
Assuming a raw water with 60 mg Pt/l colour (at pH 6) and 6,7 mg/l TOC, a coagulation efficiency of 75% would leave 15 mg Pt/l colour in the treated water. This would in most cases be considered to be acceptable. To achieve this a dosage of approximately 0,8 mg/mg TOC or 5,4 mg/l of chitosan would be sufficient.

The results are well in agreement with results reported by other investigators, as summarized in table 2-2, chapter 2.5. It is of special interest to compare the results to the results obtained in coagulation-direct filtration studies with chitosan by Eikebrokk (1999) and Saltnes (2002) as these studies were performed on the same raw water type used in this study. Eikebrokk (1999) observed highest removals of colour (samples filtrated through 0,45 μm membrane filter) and TOC of respectively 80 and 50 % at coagulation pH 6 and with a TOC-specific chitosan dosage of 1,36 mg/mg C (7,5 mg/l) using a dual media (sand-anthracite) pilot scale filter column. Saltnes (2002) using expanded clay aggregates as filter medium observed colour- and TOC removals of 80 and 37% respectively at pH 6, but with a lower chitosan dose (0,73 mg/mg C corresponding to 4,0 mg/l). The levels of removal observed with the experimental protocol used in this study are in agreement with those of Eikebrokk and Saltnes.

Experiments performed for reference purposes showed (chapter 5.1.2) that with iron chloride sulphate as coagulant removals of colour close to 100% and of TOC approximately 75% at a dosage of 7 mg Fe/l, however requiring a coagulation pH between 4,5 and 5,5. This shows that cationic polyelectrolyte coagulants are capable of achieving more or less the same level of colour removal at pH 6,0 as iron chloride sulphate at pH 4,5-5,5, but that maximal obtainable removals with respect to TOC lies at considerable lower level for polyelectrolytes than for iron chloride sulphate. In principal this agrees well with findings reported by Edzwald et al (1987), Eikebrokk (1999) and Saltnes (2002), as referred in chapter 2.5.1.3.

Saltnes (2002) proposes that the higher TOC removal observed with metal salt coagulants than with chitosan is due to polymer-residues in the coagulated and filtrated water. Evidence to prove this hypothesis right or wrong has not been established in this study. However some simple calculations can be performed to evaluate this hypothesis:

At 90 % colour removal using approximately 2,0 mg/mg TOC or 13 mg/l chitosan, approximately 40% TOC removal is achieved, leaving approximately 4 mg/l dissolved TOC in the water. With iron chloride sulphate the same colour removal level results in approximately 70% removal with respect to TOC, leaving approximately 2 mg C/l dissolved TOC in the water. In other words using chitosan to achieve 90% colour removal leaves 2 mg/l more dissolved TOC in the water than using iron chloride sulphate. TOC-analysis performed on a diluted chitosan solution showed that 1 mg chitosan had a TOC value of 0,42 mg C/l. If the "extra" 2 mg C/l of dissolved TOC left in the water coagulated with chitosan were to be attributed only to residual dissolved chitosan, this would correspond to a dissolved residual of approximately 4,8 mg/l chitosan, or close to 40% of the total amount of chitosan dosed. Intuitively this number appears to be unreasonably high, making it unlikely that the difference in TOC removal observed with chitosan relative to iron chloride sulphate can be solely attributed to residual dissolved chitosan in the coagulated water.

The upper left part of figure 5.3 indicates clearly that the coagulation efficiency per mg polyelectrolyte dosed (measured as removal of coloured and UVA substances) observed for the different polymers is divided in two groups; PDADMAC and poly-Epi-amine exhibiting higher dose efficiencies than chitosan and the two CPAAMs. This tendency does not appear to apply with respect to the overall removal of NOM measured as removal TOC. However, keeping in mind the lower repeatability and reproducibility observed for TOC removal, it is not justified to draw conclusions with respect to differences in maximal removal and dose efficiency among the polyelectrolytes tested. Consulting the polymer properties (table 4-1) in chapter 4.1, the grouping of the polyelectrolytes with respect to coagulation dose efficiency is seen to coincide with a grouping in charge densities. PDADMAC and poly-Epi-amine have charge densities of 6,2 and 7,0 meq/g respectively whereas the three latter have charge densities in the region 4,0 to 4,5 meq/g.

This shows that polymer charge density plays a major role in the formation of NOM-polymer aggregates. A more elaborate analysis and discussion with regards to this effect is offered in chapter 5.1.4 and shows that the differences in polyelectrolyte efficiency with respect to coagulation of humic substances is predominantly an effect of polyelectrolyte charge density, and furthermore that the effect of charge density is a result of different dosages of cationic charge equivalents and not the result of differences in the spatial distribution of cationic charges along the polymer chains.

The medium molecular weight (MMW) CPAAM was included in the test set to investigate if molecular weight had any effect on CPAAMs efficiencies as coagulant for NOM. The results as presented in figure 5.3, comparing low molecular weight (LMW) and medium molecular weight (MMW) CPAAMs indicate no positive effect of increased molecular weight on coagulation efficiencies.

Considering coagulation performance over the entire dosage range (upper left and right and lower left part of figure 5.3) PDADMAC, poly-Epi-amine and LMW CPAAM all show clear maxima and overdosage with respect to all parameters, whereas chitosan and MMW CPAAM do not show this feature. This overdosing, or restabilisation, may be explained with lack of aggregate formation or formation of very small (< 0,1 µm), non-flocculating aggregates. In retrospect this should have been investigated further by checking presence of particles (measuring turbidity or optical density) in the samples. Whereas the reductions in removals of colour and UVA in the overdosed region with respect to PDADMAC, poly-Epi-amine and LMW CPAAM may be explained by the presence of small aggregates (< 0,1 µm) exerting optical density, large negative removals in TOC can only be explained by the presence of excessive polymer residuals (in dissolved or aggregated forms). Although these phenomena occur at dosage levels that are unlikely to be used in a practical situation and therefore are of minor interest from a practical point of view, it is, however, interesting to notice that neither overdosage (or restabilisation) nor negative removals with respect to dissolved TOC is observed with chitosan or MMW CPAAM.

5.1.3.2 Comparison of dosage responses with respect to colour, UVA and TOC

Coagulation dosage responses of coloured and UV-absorbing NOM relative to the bulk of the NOM (measured as TOC) are presented as removals after filtration through 0,1 µm membrane filter as function of TOC-specific polymer dose in figure 5.4.

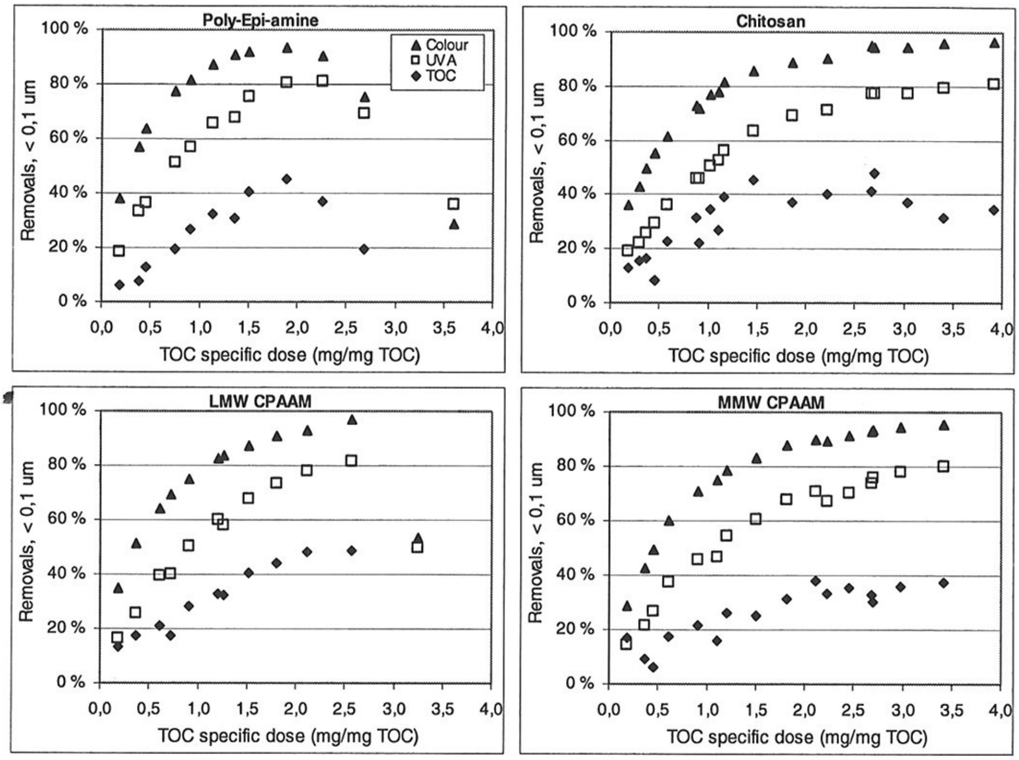


Figure 5.4. Comparison of relative removals of UV-absorbing substances (UVA), total organic carbon (TOC) and colour from humic water as function of TOC specific polymer dose (mg/l polymer added divided by mg C/l TOC in unfiltered raw water) after coagulation, flocculation and final filtration through 0,1μm membrane filter.

Figure 5.4 shows in general that apart from a relatively parallel displacement with respect to removal levels, the dosage responses with respect to coagulation of coloured, UV-absorbing and bulk NOM (measured as TOC) are very similar.

Removals of coloured NOM are generally higher than removals of UV-absorbing NOM which again are higher than removals of TOC, the average ratio being 1: 0,7 : 0,3 for colour, UVA and TOC respectively.

Poly-Epi-amine and PDADMAC exhibit very similar patterns (demonstrated in appendix D) and are therefore only represented by poly-Epi-amine in this compilation. Dosage responses with respect to coagulation of, UVA and bulk NOM (measured as TOC) with PDADMAC and poly-Epi-amine are well related over the whole dosage range and show coinciding maxima. Also with chitosan the dosage responses with respect to aggregate formations of coloured, UVA and bulk NOM (measured as TOC) are well related. However, contrary to the dosage response observed for PDADMAC and poly-Epi-amine, there are no clear maxima with respect to NOM removals for chitosan, but rather a break in the curves. These breaks occur at the same dosage with respect to coagulation of colour, UVA and TOC. At dosages above these break points removals of colour and UVA continue to increase (although modestly) whereas removal of TOC flattens out. LMW CPAAM also exhibits related dosage responses with respect to removals of coloured, UV-absorbing and bulk NOM (measured as TOC). The responses are similar to those of PDADMAC and poly-Epi-amine. There are distinct points of maximum removal followed by steep declines at dosages above these points. Dosage responses for coagulation with MMW CPAAM are also related, but removal of colour and UVA continues to increase after TOC removal has reached its maximum. As with chitosan, no clear maxima points, nor regions of overdosage, are observed.

5.1.3.3 Flocculation of NOM-polyelectrolyte aggregates

The experimental protocol has, as described in chapter 4, included filtration of all samples through 11 μm paper filter directly after flocculation followed by filtration through 1,2 μm, 0,45 μm and 0,1 μm membrane filters in sequence and with collection of sample aliquots after each filtration. With a few exceptions all sample aliquots have been analysed with respect to colour, UVA and TOC. By comparing results after filtration through 0,1 μm membrane filters (assumed to reflect the systems coagulation state) with results after filtration through filters with larger pore sizes (cutting off larger flocs) it is possible to evaluate also the floc forming properties of the aggregates formed by coagulation.

Interpretations of flocculation results have been restricted to qualitative evaluations of a given systems ability to produce flocs withheld by the various pore sizes relative to the degree of coagulation (amount of aggregates formed) in the system. A system reaching a high degree of coagulation as measured by removals after filtration through 0,1 μm, but failing to reach a high degree of flocculation as measured by cut off by larger pore sizes is in this manner understood to produce aggregates with poor flocculation properties.

This sub chapter is divided into two parts, the first focuses mainly on the relationship between coagulation of dissolved organic substances and flocculation of the formed aggregates whereas the second is intended to offer a more direct comparison of flocculation properties of the aggregates formed by coagulation with the different polyelectrolytes.

The relationship between coagulation of dissolved organic substances and flocculation of aggregates

Analysis of sample aliquots filtered through 11 µm paper filter, and 1,2 and 0,45 µm membrane filter have been used to assess flocculation properties of the NOM-polymer aggregates resulting from coagulation. Using results from coagulation experiments with PDADMAC and chitosan as examples, relative removal of colour from humic water as function of TOC specific polymer dose after coagulation and serial filtration through filters with pore sizes 11, 1,2, 0,45 and 0,1 µm are presented in figure 5.5 below.

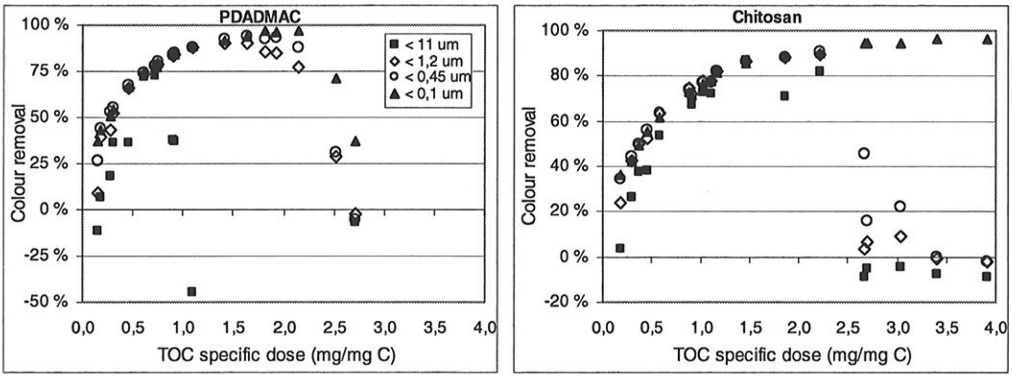


Figure 5.5. Relative removal of colour from humic water as function of TOC specific polymer dose after coagulation and serial filtration through filters with pore sizes 11, 1,2, 0,45 and 0,1 µm. The legend denominates the filter pore sizes through which the sample aliquotes have passed before measurement (including raw water)

In general figure 5.5 shows that the observed dosage responses are dependent on the final filter pore size, or in a practical situation, the particle separation method at hand. The dosage response for formation of NOM-polymer aggregates (measured as removal after final filtration through 0,1 µm membrane filter) deviates significantly from the dosage response observed with respect to the flocculation properties of the formed aggregates. This is observed most clearly by comparing the dosages at which maxima are observed with respect to removal after filtration through 11 µm paper filter relative to removal after filtration through 0,1 µm membrane filter. The optimal dosages with respect to removal after filtration through 11 μm lie substantially lower than dosages necessary to achieve maximum coagulation.

This clearly supports hypothesis A, stated in sub chapter 3.1, that coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima. In other words, the polyelectrolyte dosage providing maximal coagulation of dissolved organic substances lies substantially higher than the dosage providing aggregates with the best flocculation properties.

Removal after filtration through 11 μm has been chosen to demonstrate the difference in dosage response with respect to flocculation properties of the formed aggregates relative to the dosage response with respect to coagulation. It must however, be stressed that this does not imply that dosage optima observed with respect to removal after filtration through 11 μm can be used to locate optimal dosage for every practical particle separation method.

It is also interesting to notice that over a wide (but not the whole) range of the dosage region using 0,45 μm membrane filters gives the same removal results, and describes the coagulation state of the system just as well, as using 0,1 μm membrane. This has significant practical consequences as the use of 0,1 μm membrane filters is much more time consuming and cumbersome than filtration through 0,45 μm membrane filter.

Figure 5.6 (below) shows the relationship between coagulation of NOM (measured as colour) and the flocculation properties of the formed aggregates measured as removal of colour and residual turbidity after filtration through 11 μm paper filter.

For all polyelectrolytes tested the dosage providing maximal coagulation of dissolved organic substances is not identical to the dosage providing aggregates with the best flocculation properties measured as removal after filtration through 11 μm paper filter. However optimal dosages with respect to removal after filtration through 11 μm and removal levels at this pore size differ significantly for the different polyelectrolytes. This will be investigated in more detail later. As an alternative approach to monitoring flocculation properties of aggregates relative to the aggregate formation itself figure 5.6 includes results on residual turbidity measured after filtration through11 μm paper filter. Also in this respect the different polyelectrolytes exhibit different performances.

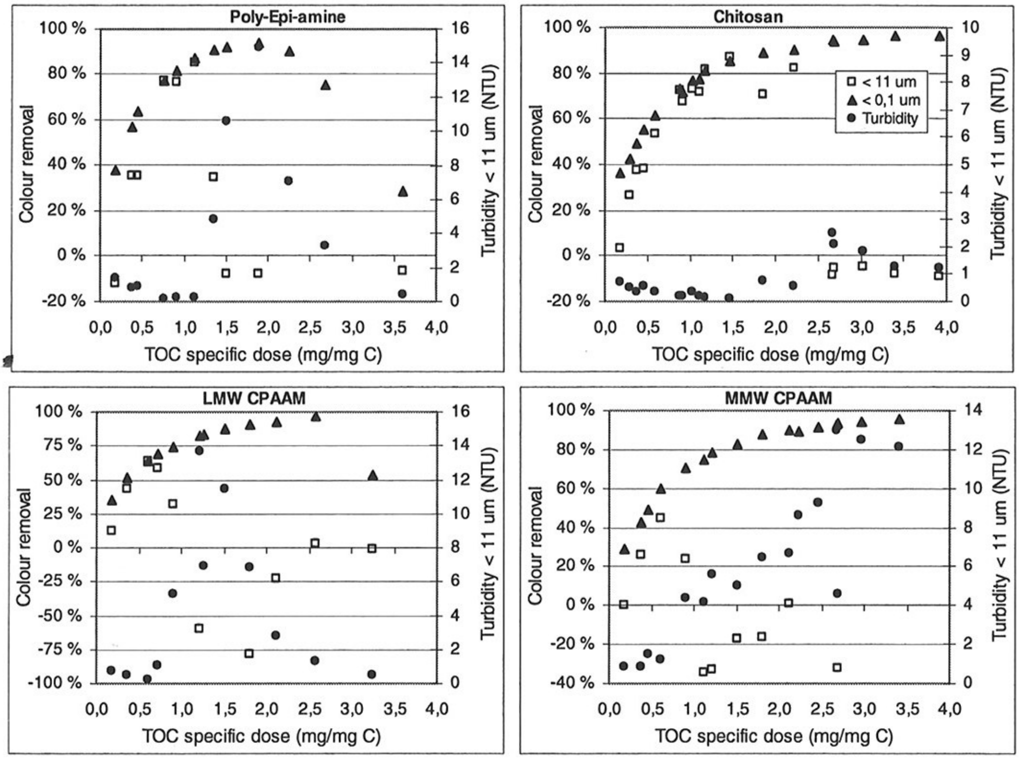


Figure 5.6. Relationship between coagulation of NOM (removal of colour after filtration through 0,1 μm membrane filter) and the flocculation properties of the formed aggregates measured as removal of colour and residual turbidity (right hand abcissa) after filtration through 11 μm paper filter.

Poly-Epi-amine and PDADMAC exhibit very similar patterns (demonstrated in appendix D) and are therefore only represented by poly-Epi-amine in this compilation. They both show that the maxima observed for coagulation of NOM coincide with the maxima observed for turbidity after coarse filtration (11 μm). With chitosan it was shown in the previous sub chapter (5.1.3.2) that contrary to the dosage response observed for PDADMAC and poly-Epi-amine, there is no clear maximum with respect to coagulation of NOM, but rather a break in the curves. These breaks do not coincide with the dosage giving maximum formation of turbidity. Instead the break points in the curves coincide with the minimum point with respect to residual turbidity. Figure 5.6 also shows that chitosan distinguishes itself from the synthetic polyelectrolytes by the fact that the highest observed residual turbidity after coarse filtration is much lower (3-5 times).

This appears to suggest that at dosages necessary to achieve maximum coagulation of NOM, the flocculation properties of aggregates formed with chitosan diverts markedly from those formed with the other polyelectrolytes.

LMW CPAAM exhibits a dosage response with respect coagulation of NOM that is similar to those of PDADMAC and poly-Epi-amine. There is a distinct point of maximum coagulation followed by a steep decline at dosages above this point. However, unlike PDADMAC and poly-Epi-amine, the optimal dose with respect to turbidity formation (approximately 1,3 mg/mg C) does not coincide with the dose giving maximum removal of NOM (approximately 2,6 mg/mg C). With respect to formation of residual turbidity MMW CPAAM, as opposed to the other polyelectrolytes tested, exhibits no maximum points in the dosing range tested. Residual turbidity rather continues to increase over the entire dosage range.

Comparison of flocculation dosage responses of the different polyelectrolytes

As was stated in the introduction to this sub chapter (5.1.3.3), interpretations of flocculation results have been restricted to qualitative evaluations of a given systems ability to produce flocs withheld by the various pore sizes relative to the degree of coagulation (amount of aggregates formed) in the system. A system reaching a high degree of coagulation as measured by removals after filtration through 0,1 μm, but failing to reach a high degree of flocculation as measured by cut off by larger pore sizes is in this manner understood to produce aggregates with poor flocculation properties.

Removals after final filtration through 11 μm, together with residual turbidity results, lend themselves most conveniently with respect to monitoring flocculation properties of NOM-polymer aggregates and were therefore chosen as the general method of presentation flocculation properties. Comparisons of flocculation properties of aggregates formed by coagulation of NOM with the different polyelectrolytes tested are presented in figure 5.7.

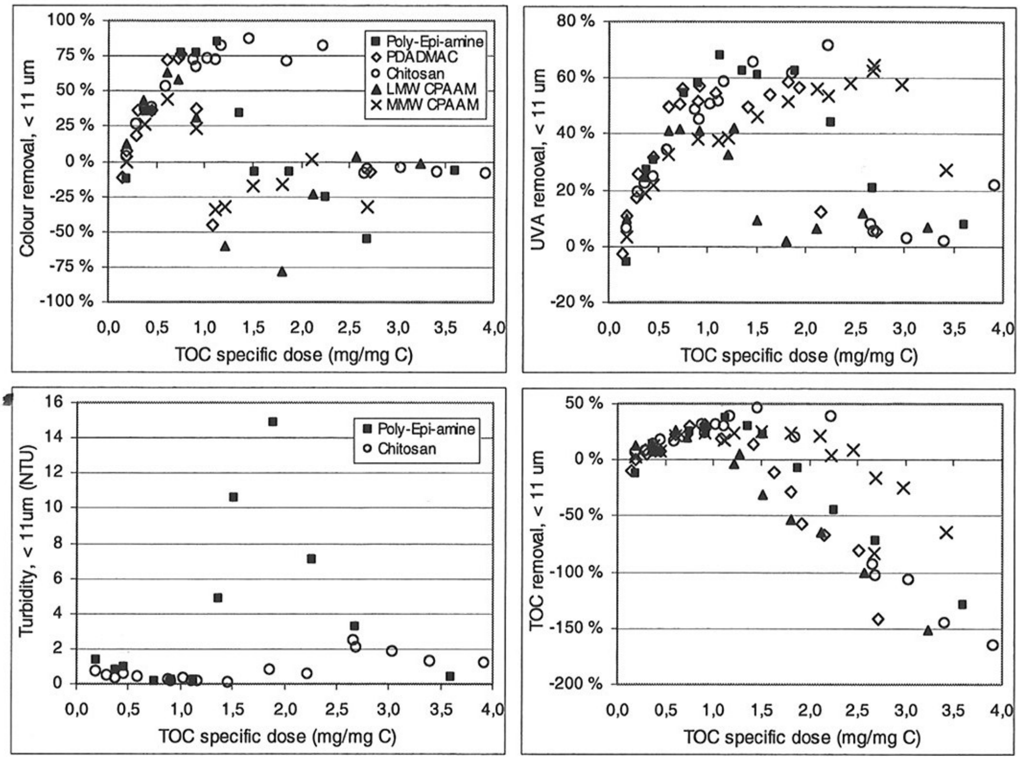


Figure 5.7. Comparison of flocculation dosage responses of the different polyelectrolytes measured as removals of NOM and residual turbidity after final filtration through 11 μm paper filter as function of TOC specific polyemr dose.

Figure 5.7 shows that at low dosages (up to approximately 0,7 mg/mg TOC or up to approximately 4,7 mg/l) all polyelectrolytes tested show comparable removals of colour, UVA and TOC after filtration through 11 μm paper filter. At dosages above this significant differences appear between the different polyelectrolytes. It is especially interesting to notice the results obtained with chitosan and LMW CPAAM as coagulants. Systems coagulated with chitosan appear to reach high levels of removal over a wider dosage range than the other polyelectrolytes, whereas with LMW CPAAM removals reach a maximum at a substantially lower dosage and removal level than the other polyelectrolytes. This seems to indicate that NOM aggregates formed by coagulation with chitosan have better flocculation properties at high dosages.

Figure 5.7 shows that there are substantial differences between the polyelectrolytes with respect to the ability to create flocs larger than 11 μm. Chitosan and poly-Epi-amine show the highest observed removals of colour and

UVA (approximately 85 and 70% respectively for colour and UVA). Second highest is PDADMAC (73 and 57%) followed by LMW CPAAM (64 and 42%). MMW CPAAM shows the lowest removal of colour (45%), but a more complex behaviour with respect to UVA-removal, first appearing to reach a maximum at about 40% removal, then climbing further to a removal of 64%. It is interesting to notice that if only the strong, low molecular weight polyelectrolytes are considered, the internal ranking with respect to highest observed removals appear to correspond with the ranking with respect to charge density (poly-Epi-amine > PDADMAC > LMW CPAAM). This is consistent with the findings of Kam and Gregory (2001) for CPAAMs with different charge densities and will be discussed in more detail in sub chapter 5.1.4. However, also in this line of reasoning chitosan stands out, exhibiting far better floc-forming properties than its charge density would suggest.

Residual turbidity after filtration through 11 μm gives a rough indication of the amount of coagulated matter unable to produce large flocs and is therefore also useful in order to interpret the results with respect to the flocculation properties of formed aggregates. The most interesting difference with respect to turbidity formation (lower left part of figure 5.7) is for reasons of lucidity exemplified with chitosan and poly-Epi-amine. (Turbidity results for all polyelectrolytes are presented in appendix D). Whereas coagulation of NOM with the synthetic polyelectrolytes (represented by poly-Epi-amine) at dosages higher than 0,6 to 1,0 mg/mg TOC is accompanied by high residual turbidity after filtration through 11 μm, coagulation with chitosan results in turbidity values that in general are much lower (3-5 times). Visual observations conducted during the experiments confirm these findings.

It appears that chitosan produces aggregates with NOM with better flocculation properties than the synthetic polyelectrolytes tested.

Flocculation properties of aggregates formed by the different polyelectrolytes will be discussed further in light of electrical charge conditions in sub chapter 5.1.4.

5.1.4 Effect of polyelectrolyte charge density on coagulation and flocculation of NOM

The results presented in this chapter are not based on separate experiments, but on a simple mathematical transformation of the x-axis of results presented in the previous chapter (5.1.3).

The polyelectrolytes chosen for this study comprises polymers with different chemical composition as well as differences in polymer charge density. From the literature it is clear that polyelectrolyte charge density is of great importance with respect to coagulation of NOM. The results presented in the previous chapter also point in that direction. However, analysing results as function of polymer dose makes it impossible to separate between the effects of polyelectrolyte charge density (spatial distribution of charge along the polymer chain) as such and the effects of merely adding more charge equivalents to the system per mg polymer added when using a polyelectrolyte with higher charge density. This separation can be achieved by recalculating dosages to give micro equivalents (μeq) of cationic charge added instead of mg polymer added simply by dividing the latter by the stoichiometric charge density (μeq/mg polymer) of the polyelectrolytes. Plotting removals as function of μeq cationic charge added will now reflect the effect of the chemical composition of the polyelectrolyte itself, including spatial distribution of charge, on its efficiency as a coagulant for NOM. It is not possible to distinguish between the effects of chemical composition relative to those of charge density directly. However it will be demonstrated that, in some cases, the results obtained can be used indirectly to separate even between the effects of charge density relative to those of chemical composition.

5.1.4.1 Effect of polyelectrolyte charge density on coagulation of NOM

The initial treatment of the NOM-coagulant formation capabilities of the different polyelectrolytes (chapter 5.1.3) indicated that charge appeared to be of major importance in the coagulation of coloured and UVA substances in the humic water studied. The conclusions were that although all the polyelectrolytes converged towards approximately the same maximum removals of colour and UVA after final filtration through 0,1 μm, there was a clear division in dosage efficiency that coincided with a division in polyelectrolytes charge density. This could be the result of a relatively higher dosage of cationic charge equivalents for polymers with a higher charge density or an effect of differences in spacing between cationic groups on the polymer main chain. In order to investigate this polymer dosages have been recalculated to dosages in form of cationic charge equivalents and removals have been plotted as function of the latter in figure 5.8.

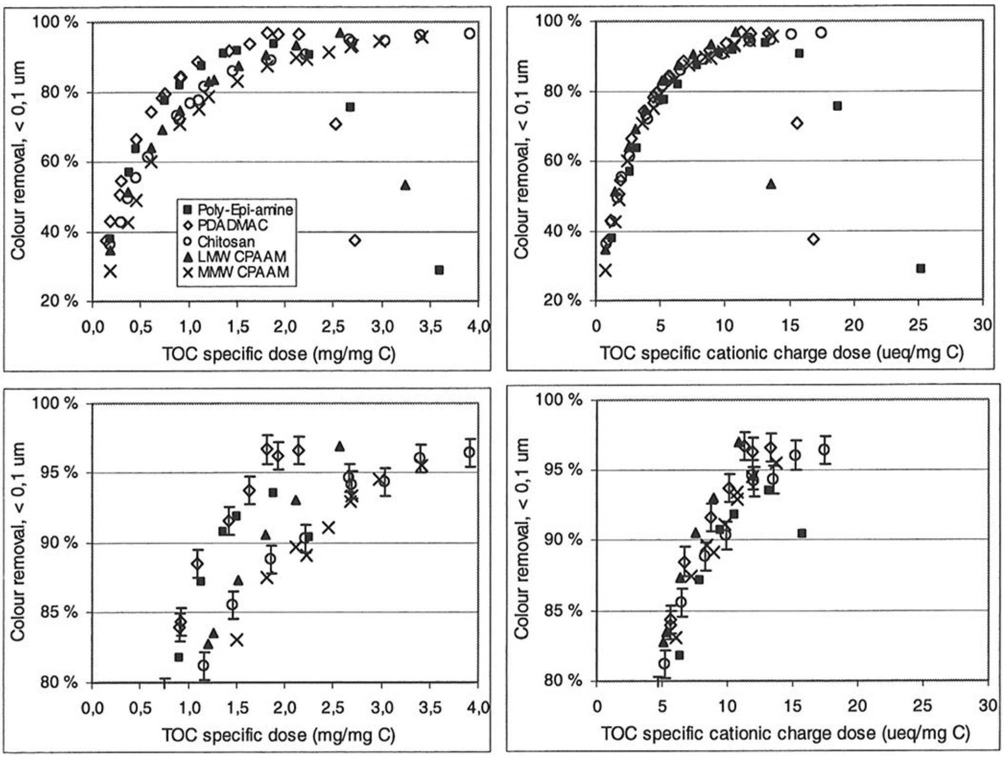


Figure 5.8. Comparison of removal efficiencies of different cationic polymers as function of polymer dose vs. cationic charge equivalents dose after coagulation and final filtration through 0,1 μm pore size membrane filter. **Left:** Relative removal of colour from humic water as function of TOC specific polymer dose (mg/l polymer added divided by mg C/l TOC in raw water). **Right:** Relative removal of colour from humic water as function of TOC specific dose of cationic charge (μeq/l cationic charge added as polymer divided by mg C/l TOC in raw water). Error bars (for lucidity only included for PDADMAC and chitosan) in lower graphs indicate total experimental uncertainty of individual data points estimated as described in chapter 4.6.1.

Inspection of the upper graphs in figure 5.8, comparing colour removal as function of TOC specific polymer dose (left) to removal as function of TOC specific cationic charge dose (right), that there appears to be no significant differences in the dose efficiencies with respect to coagulation of coloured substances when differences in charge densities are compensated for.

This clearly indicates that the higher dose efficiency observed for PDADMAC and poly-Epi-amine over chitosan and the two CPAAMs is merely an effect of higher dosage of cationic charge.

It is also interesting to notice that for the strong polycations (except MMW CPAAM) the onset of overdosage or restabilisation appear to coincide at the same TOC specific cationic charge dose of 12 ± 1 μeq/mg TOC.

Comparing the enlargements of the upper graphs (lower left with lower right) of figure 5.8 confirms that the higher polymer dose efficiency observed for PDADMAC and poly-Epi-amine is caused by a correspondingly higher dosage of cationic charge equivalents. However, focusing only on the lower right (colour removal as function of specific cationic charge dose) it appears that there are in fact probably significant, although small, differences in dose efficiencies, also when the differences in charge densities are compensated for. LMW CPAAM and PDADMAC show somewhat higher cationic charge dose efficiency than poly-Epi-amine, chitosan and MMW CPAAM (which all show more or less the same dose efficiency). The same effects were observed with respect to coagulation measured as removal of UVA as function of TOC specific polymer dose versus TOC specific cationic charge dose.

Reconsidering the charge densities (4,2 and 6,2 meq/g for LMW CPAAM and PDADMAC respectively versus 7,0, 4,5 and 4,0 meq/g for poly-Epi-amine, chitosan and MMW CPAAM), it is unlikely that this difference is due to charge densities only. Had this been the case one would expect the results obtained with poly-Epi-amine to group with those of PDADMAC (and LMW CPAAM with chitosan). Nor does it seem plausible that this reflect an effect of differences in molecular weight as molecular weights of PDADMAC and poly-Epi-amine are reported (by the manufacturers) to be more or less identical. The results therefore appeared to indicate that at least the chemical composition of PDADMAC is more favourable with respect to coagulation of NOM than that of poly-Epi-amine. Assuming that molecular weight is of minor importance it should be feasible to make the same statement with respect to the difference observed between LMW CPAAM and chitosan, favouring the chemical composition of the prior. Bolto *et al* (1998) have suggested that different efficiencies of polyelectrolytes as coagulants for NOM may be related to differences in polarity of the carbons in the main chains, efficiency increasing with decreasing polarity. In the literature search (chapter 2) no reports were found that specifically addressed this issue. However, the differences pointed out above with respect to cationic charge dose efficiency appear to be in accordance with this hypothesis.

The magnitudes of these possible effects of the composition of the polyelectrolyte backbones are, however, noticeably smaller than the effects that can be attributed to the mere addition of cationic charge.

5.1.4.2 Effect of polyelectrolyte charge density on flocculation

Whereas the coagulation of dissolved organic substances seemed to be controlled by dosage of charge equivalents, figure 5.9 shows that the picture appears to be more complex with respect to the ability of the aggregates to grow to flocs.

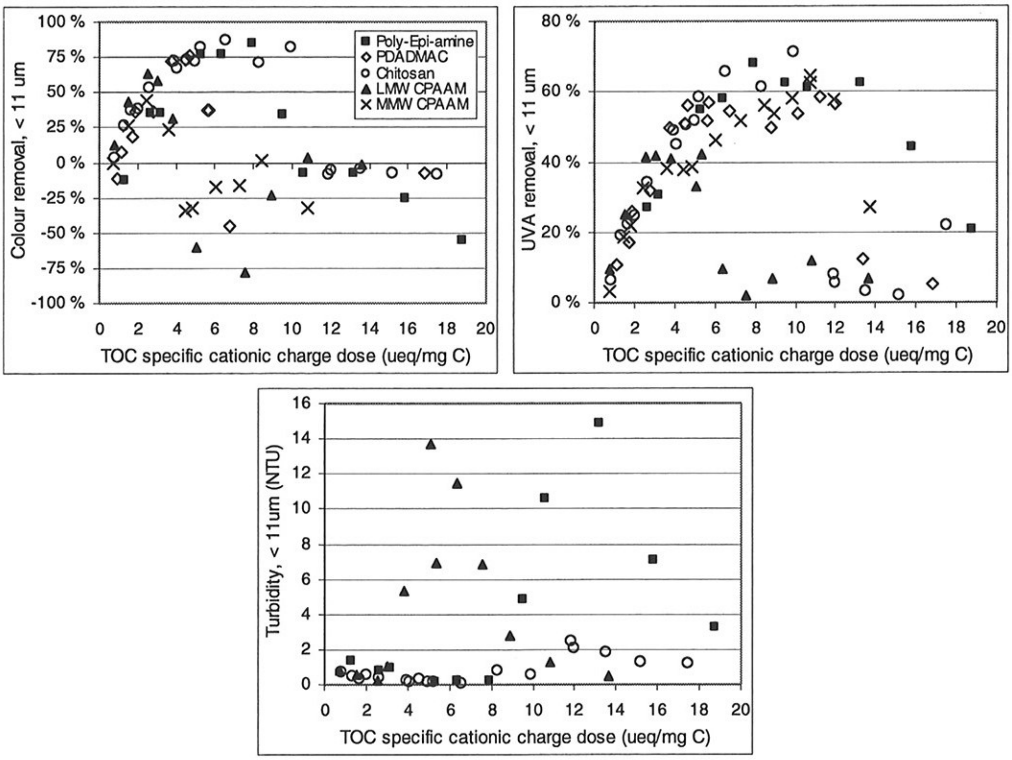


Figure 5.9. Comparison of residual turbidity and removals of NOM after final filtration through 11μm pore size paper filter as function of TOC specific cationic charge dose.

Considering first the removal of colour and UVA after filtration through 11 μm paper filter (upper part of figure 5.9) it is seen that polymer performance cannot be explained to the same extent as for coagulation by mere dosage of cationic charge equivalents. Both maximum achieved removals as well as onset of overdosage or restabilisation differs significantly with respect to cationic charge dosed for the different polyelectrolytes. This is illustrated specifically in figure 5.10.

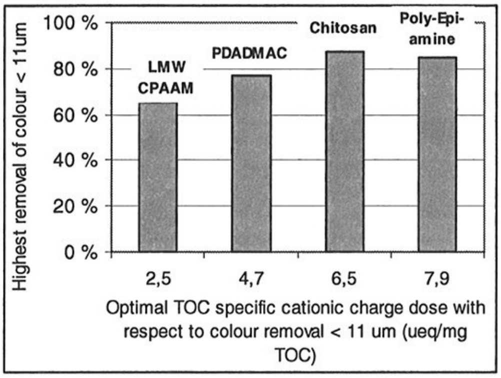


Figure 5.10. Highest observed removals of colour after filtration through 11 μm and corresponding TOC specific polymer doses expressed as dosage of cationic charge equivalents.

For LMW CPAAM maximum colour removal is reached at a dose of cationic charge equivalents of 2,5 μeq/mg TOC with a corresponding removal of 65%. For PDADMAC, chitosan and poly-Epi-amine the corresponding numbers are 4,7 μeq/mg TOC – 77%, 6,5 μeq/mg TOC – 87% and 7,9 μeq/mg TOC – 85% respectively.

In other words, optimal dose for floc growth of NOM-polymer aggregates appears not to be governed by cationic charge dose, but rather by the chemical composition of the polyelectrolytes.

As was pointed out earlier (5.1.3), if only the strong, low molecular weight polyelectrolytes are considered, the internal ranking with respect to highest observed colour removals appear to correspond with the ranking with respect to charge density (poly-Epi-amine > PDADMAC > LMW CPAAM). However, in this line of reasoning chitosan stands out, exhibiting far better floc-forming properties than its charge density would suggest.

As was pointed out earlier, one of the most interesting findings with respect to the flocculation properties of NOM-polymer aggregates is the substantially lower production of turbidity, and broader dosage range giving good removal after filtration through 11 μm, associated with the use of chitosan as a coagulant. An important question seems to be whether this can be explained by differences in additions of cationic charge equivalents. The lower part of figure 5.9 shows that, except for LMW CPAAM, all polyelectrolytes (exemplified by poly-Epi-amine and chitosan, full presentation is given in appendix D) exhibit maximal residual turbidity at approximately the same cationic charge dose of 12 ± 1 μeq/mg TOC. This dose is identical with the dose observed giving maximum coagulation (removal after filtration through 0,1 μm) for the strong polycations (except MMW CPAAM). LMW CPAAM appears to constitute a special case with respect to flocculation properties of aggregates and formation of residual turbidity, reaching a maximum at a significantly lower dose of cationic charge equivalents than the other polyelectrolytes.

5.1.4.3 Practical implications of the effect of polyelectrolyte charge density

In sub chapter 5.1.4.1 it was demonstrated that the coagulation efficiency of humic substances with cationic polyelectrolytes predominantly depends on the amount of cationic charge equivalents dosed per mg TOC and not on the chemical composition of the polyelectrolyte as such. When considering possible practical implications of this it must be stressed that the findings are based on experiments on only one type (or source) of humic water.

Further research should be carried out on other sources of humic water to verify or reject the possible broader validity of these findings. However, if the findings were found to be valid for humic waters from a broad selection of sources, the obvious practical implication of this finding appears to be that the best polymer for coagulation of NOM, giving the highest coagulation per mg polymer added, would be the one with the highest charge density. Furthermore, after having determined the coagulation dosage response with respect to cationic charge dose for one polyelectrolyte in a given water, it would probably be possible to predict the coagulation dosage response of any cationic polyelectrolyte (assuming that the charge density is known) for that specific water.

Sub chapter 5.1.3 demonstrated that coagulation of NOM is only one part of the total picture, and sub chapter 5.1.4.2 demonstrated that when flocculation properties of the formed aggregates are considered the polymer performances could not be explained to the same extent as for coagulation by mere dosage of cationic charge equivalents. Optimal dose for floc growth of NOM-polymer aggregates appeared not to be governed by cationic charge dose, but rather by the chemical composition of the polyelectrolytes. Therefore further research into the effect of polyelectrolyte charge density and the possible practical applicability of this should also include realistic particles separation techniques such as dissolved air flotation or depth filtration.

5.1.5 Main findings on coagulation and flocculation of humic substances (pH 6)

- All polyelectrolytes tested were efficient in coagulating NOM (measured as removal of dissolved NOM after filtration through 0,1 µm membrane filter) and reached approximately the same maximum levels of coagulation.

- Colour removals after filtration through 0,1 µm up to 95% were observed for all polyelectrolytes. TOC removals were lower reaching a maximum of 45-50%.

- High dosages (10 to 20 mg/l) were required to achieve maximum coagulation of NOM, but coagulation levels adequate for most practical purposes (65 to 85%) could be achieved with substantially lower dosages (approximately 3 to 7 mg/l).

- For all polyelectrolytes, the dosage responses with respect to coagulation of coloured, UV-absorbing and bulk NOM (measured as TOC) were very similar

- Differences in coagulation dose efficiency (% NOM coagulated per mg polymer) between the different polyelectrolytes were primarily an effect of differences in polyelectrolyte charge density. This supports hypothesis B, chapter 3.1.

- The effect of polyelectrolyte charge density on coagulation of coloured and UV-absorbing NOM were explained by the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not by the differences in the spatial distribution of charge as such. This supports hypothesis C, chapter 3.1.

- The results on low molecular weight CPAAM compared to those of medium molecular weight CPAAM indicated no positive effect of increased molecular weight on coagulation efficiencies. This supports hypothesis D, chapter 3.1.

- Coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates were shown to be two distinguishable processes with distinguishable dosage optima. The polyelectrolyte dosage providing maximal coagulation of dissolved organic substances lies substantially higher than the dosage providing aggregates with the best flocculation properties. This supports hypothesis A, chapter 3.1.

- Optimal dose for floc growth of NOM-polymer aggregates appeared not to be governed by cationic charge dose, but rather by the chemical composition of the polyelectrolytes.

- The results showed substantial differences between the polyelectrolytes with respect to the ability to create flocs larger than 11 μm. With the exception of chitosan, the highest observed removal after filtration through 11 μm for each polyelectrolyte appeared to follow the same internal ranking as the polyelectrolyte charge densities (poly-Epi-amine > PDADMAC > CPAAM).

- Chitosan appeared to produce aggregates with NOM with better flocculation properties than the other polyelectrolytes tested.

5.2 Effect of pH on coagulation and flocculation

The objective of the experiments reported in this chapter has been to evaluate the effect of pH on coagulation and flocculation of NOM with polyelectrolytes. It has been of special interest to examine the effect of pH on coagulation with a strong cationic polyelectrolyte relative to a weak (charge depending on pH) cationic polyelectrolyte. PDADMAC having a quaternary ammonium cationic group was chosen as a strong polycation. Chitosan, receiving its cationic charge from pH-dependent protonation of the amine-group, is a weak polycation. In addition to the chitosan (F_A 0,05) used earlier in this study the effect of pH was also tested for a chitosan with degree of acetylation (F_A) of 0,37. This sub chapter will focus on the results obtained with PDADMAC and the "standard" chitosan (F_A= 0,05) that was also used in the main experiments on humic water and wastewater. Results on the more highly acetylated chitosan (F_A = 0,37) will be reported in sub chapter 5.3 (Effect of the degree of acetylation in chitosans).

In sub chapter 3.1 hypothesis E was stated to predict the effect of pH:

E **The effect of pH on coagulation of dissolved humic substances with cationic polyelectrolytes**

1) Due to increased protonation of the carboxyl groups, and thus reduced anionic charge density, of the humic substances, lowering of pH from 6 to 4 results in improved dose efficiencies with respect to coagulation of NOM with cationic polyelectrolytes.

2) With chitosan a reduction of pH will also result in a gain in cationic charge density due to protonation of the amine groups. Therefore the effect of reducing pH on polymer dose efficiency will be more pronounced for a weak polycation such as chitosan than for a strong polycation such as PDADMAC.

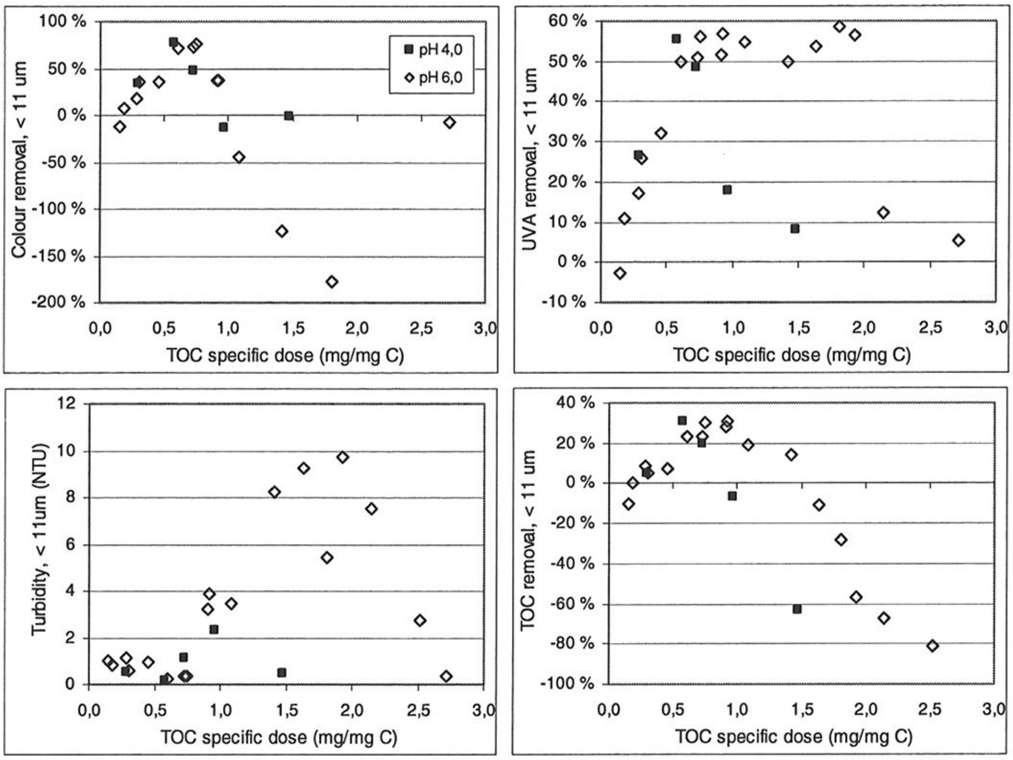


Figure 5.12. Effect of pH on flocculation properties of NOM-polymer aggregtaes after coagulation with PDADMAC. Comparison of residual turbidity and removals of NOM after final filtration through 11μm pore size paper filter as function of TOC specific polyemr dose.

Focusing on the upper left part of figure 5.12 it seems that adjusting pH from 6 to 4 has a far weaker effect on removal of colour after filtration through 11 μm paper filter than on the actual coagulation of NOM by PDADMAC (removal after filtration through 0,1 μm). Maximum removal remains the same and optimal dosage with respect to maximal removal is shifted only slightly towards a lower dosage at pH 4. Measuring on UVA and TOC removal after filtration through 11 μm the same tendency is seen with respect to maximal achievable removals. With respect to UVA and TOC removals the dosage regions resulting in given removal levels become narrower at pH 4 than at pH 6.

The lower left part of figure 5.12 shows the effect of lowering pH on formation of residual turbidity after filtration through 11 μm. The highest observed residual turbidity is much lower at pH 4 than at pH 6 and occurs at a substantially lower polymer dose (approximately 1,0 mg/mg TOC at pH 4 as opposed to approximately 2,0 at pH 6). In sub chapter 5.1.3 it was demonstrated that at dosages necessary to achieve maximum coagulation of NOM, coagulation was accompanied by high residual turbidity after filtration through 11 µm. Furthermore, the dosage giving the highest observed coagulation coincided with the dosage giving the highest residual turbidity.

Comparing figures 5.12 (bottom left part) and figure 5.11, the same pattern is observed at pH 4. It is also interesting to notice that the amount of turbidity formed at dosages giving maximum coagulation is much higher at pH 6 than at pH 4 (10 NTU vs. 2,5 NTU). This seems hardly explainable by the larger amount of coloured substances coagulated at pH 6 (only 5 % higher removal after filtration through 0,1 µm) than at pH 4. However with respect to coagulation of dissolved TOC the difference in highest removal after filtration through 0,1 µm is more substantial (58% at pH 6 vs. 39% at pH 4).

In the treatment of the effect of pH on the coagulation of NOM by PDADMAC it was suggested that the reduction in highest observed coagulation as pH is reduced from 6 to 4 could be explained by the existence of a fraction within the NOM that is neutralised and rendered unable to interact electrostatically with the cationic polyelectrolyte at pH 4. In this respect the results on removals after filtration through 11 µm would suggest that this fraction also exhibits poorer flocculation properties than the fraction of NOM that is coagulated both at pH 6 and pH 4.

5.2.2 Effect of pH on coagulation and flocculation with a weak polycation (chitosan)

In the case of the weak polycation (chitosan) lowering of pH affects charge densities of both NOM and polyelectrolyte. The anionic charge density of NOM is reduced due to protonation of carboxyl groups, whereas the cationic charge density of chitosan is increased (theoretically from 4,5 to 5,6 meq/mg) due to protonation of amine groups. It is therefore plausible to expect the effect to be "double-positive" with respect to increased dose efficiency in the coagulation (aggregate formation), assuming that aggregate formation is strongly related to actual dosage of cationic charge relative to anionic charge on the NOM. In other words, one would expect to observe an even stronger effect of lowering pH for the coagulation of NOM with chitosan than for PDADMAC.

The effect of adjusting pH from 6,0 to 4,0 on coagulation of NOM with chitosan is shown as removal of colour after filtration through 0,1 μm membrane filter in figure 5.13 below. Again colour values measured at pH 4 have been corrected to values corresponding to pH 6 according to appendix C.

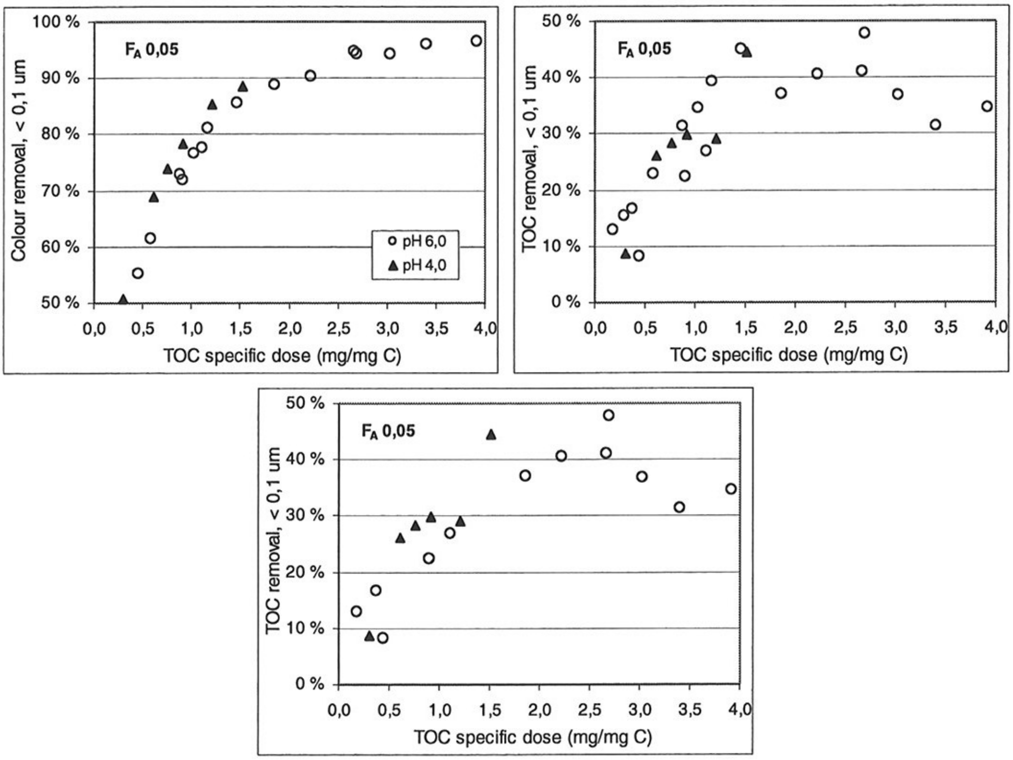


Figure 5.13. Effect of pH on coagulation of NOM with chitosan measured as removal of colour (left) and TOC (right) after final filtration through 0,1 μm membrane filter as fucntion of TOC specific polymer dose. Bottom: Results on TOC removal at pH 6 from experiment performed 05.09.01 omitted.

The left part of figure 5.13 shows that with respect to colour removal, the same tendency can be observed for chitosan with respect to increased dose efficiency was seen with PDADMAC. More colour is removed with the same polyelectrolyte dose as pH is reduced from 6 to 4. However a "double-positive" effect, originating from a simultaneous reduction in NOM anionic charge density and increase in cationic charge density on chitosan (suggested in the introduction to this sub chapter), does not appear to be evident. On the contrary, the shift towards higher dose efficiency at pH 4 is far less pronounced with chitosan than with PDADMAC. Whereas for PDADMAC the lowering of pH from 6 to 4 resulted in 10-15% higher removal of colour for the same polymer dose, the corresponding increase observed with chitosan appears to be rather small (5%). These findings appear not to support the hypothesis (E-2) predicting a more pronounced effect of lowering pH for chitosan than for PDADMAC.

With respect to coagulation measured as removal of dissolved TOC the effect of pH is unclear. As can be observed in the upper right part of figure 5.13, the results from coagulation at pH 6 (unfilled circles) exhibit poor reproducibility. The results exhibiting the highest dosage efficiency all belong to one experiment (05.09.11). In order to show this, these results have been omitted in the lower graph in figure 5.13. The results on colour removal from the same experiment (05.09.01) do not exhibit any significant deviation from the results obtained in the other experiments. Therefore all results with respect to TOC removal were checked again with special thoroughness, but it was not possible to identify analytical or experimental errors that could explain the poor reproducibility observed. The lower part of figure 5.13 shows that if the results from the experiments at pH 6 on 05.09.01 are omitted, the effect of pH is in accordance with what was observed with PDADMAC and chitosan F_A 0,37 (reported in sub chapter 5.3). However, it is not possible to conclude unambiguously with respect to the effect of pH on coagulation, measured as removal of dissolved TOC, with chitosan F_A 0,05, and further experiments should be performed to clarify this issue.

It should also be observed that due to the choice of a too narrow dosage range it is not possible to conclude on whether maximum removals after final filtration through 0,1 μm are achieved in the experiments at pH 4. It is therefore not possible to conclude on whether or not the reduction in highest achieved coagulation that was observed with PDADMAC also is the case with chitosan.

Removals after final filtration through 11 μm and residual turbidity have been chosen to illustrate the flocculation properties of NOM-polymer aggregates and are presented in figure 5.14 below.

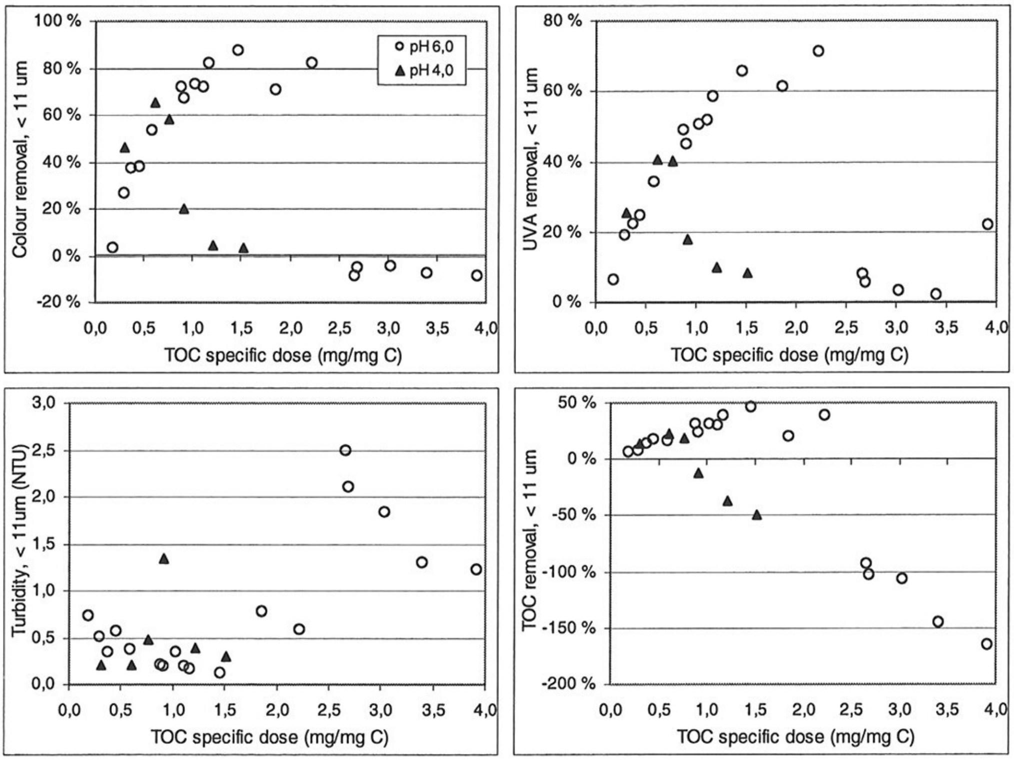


Figure 5.14. Effect of pH on flocculation properties of NOM-polymer aggregtaes after coagulation with chitosan (degree of acetylation F_A 0,05). Comparison of residual turbidity and removals of NOM after final filtration through 11μm pore size paper filter as function of TOC specific polyemr dose.

As with PDADMAC, the chitosan dose required to obtain highest observed removal is shifted towards a substantially lower dosage as pH is reduced from 6 to 4. Figure 5.14 shows however that for all parameters (colour, UVA and TOC) highest observed removals decrease substantially as pH is decreased from 6 to 4. Maximum removal of colour decreases from 90 to 60%, UVA from 70 to 40% and TOC from 50 to 25%. This differs from what was observed with PDADMAC which showed no decrease in highest observed removals as pH was reduced. For PDADMAC it was suggested that there appears to exist a fraction of NOM that is coagulating at pH 6, but not at pH 4, and that this fraction was less amenable to flocculation than the fraction of NOM that was coagulable both at pH 6 and pH 4. The data obtained in the experiments with chitosan were not sufficient to draw conclusions on this issue with respect to chitosan.

Whereas the results with PDADMAC quite clearly indicated that the lowering of pH from 6 to 4 resulted in increased polymer dose efficiency with respect to coagulation of NOM, the results with chitosan are somewhat unclear. As discussed in the introduction to this sub chapter, it was expected that the effect of pH would be stronger with chitosan than with PDADMAC. The results obtained do not support this hypothesis. On the contrary they appear to indicate that the effect of pH on coagulation of NOM with chitosan is rather insignificant. Again, the result with respect to chitosan is quite unexpected, also in light of the reports of Bolto *et al* (2001) and Saltnes (2002), both reporting on increased dose efficiency with reduced pH, and it is suggested that further experiments are performed before drawing any final conclusions.

5.2.3 Direct comparison between PDADMAC and chitosans at pH 4

For the purpose of direct comparison of PDADMAC and chitosan at pH 4, coagulation performances are presented as removals of colour and TOC as functions of TOC specific polymer dose (mg polymer/mg TOC) as well as TOC specific cationic charge dose (μeq/mg TOC) after filtration through 0,1 μm membrane filter in figure 5.15 below.

Comparisons of polymer dose efficiencies (left part of figure 5.15) show that, as at pH 6, a significant difference is observed in favour of PDADMAC over chitosan. The same tendency is seen with respect to removal of TOC, but the difference between PDADMAC and chitosan is less pronounced

Plots of removals as function of TOC specific cationic charge dose (right part of figure 5.15) indicate, as was found at pH 6, that the actual charge dose plays a role in the formation of aggregates also at pH 4. Differences in dose efficiencies between PDADMAC and the chitosans are reduced, but not eliminated.

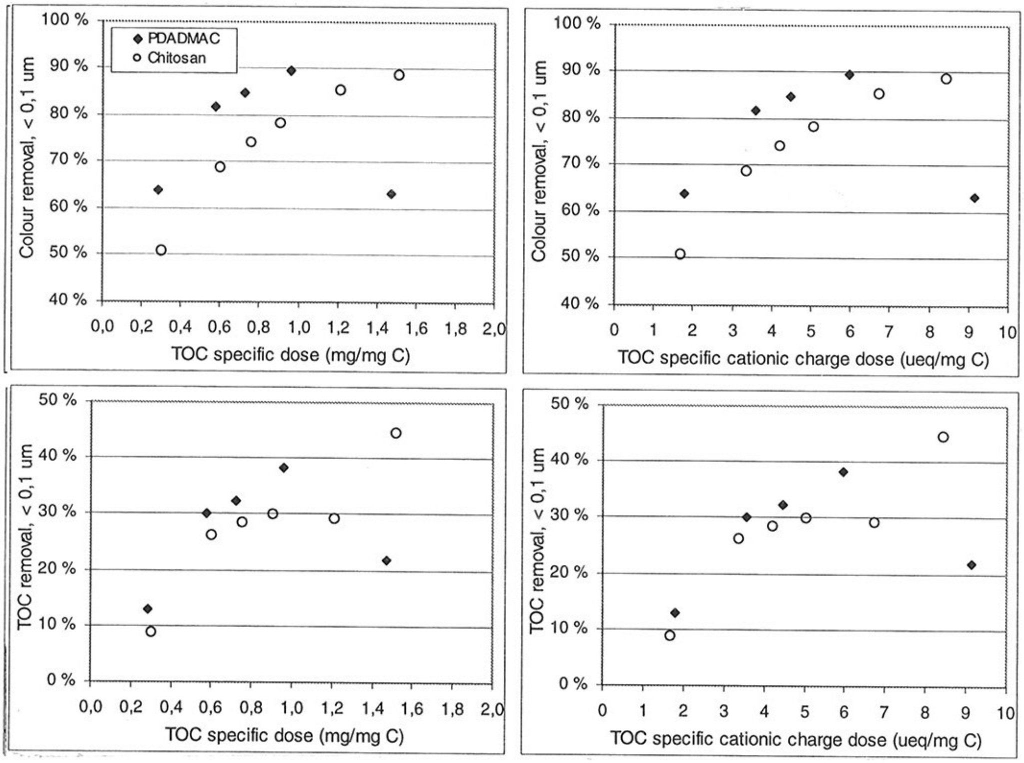


Figure 5.15. Comparison of NOM-coagulant aggregate formation in humic water by PDADMAC and chitosan (F_A = 0,05) at pH 4. Monitored as removal of NOM (measured as colour and TOC) after final filtration through 0,1 µm membrane filter. **Left:** Removals as function of TOC specific polymer dose. **Right:** Removals as function of TOC specific cationic charge dose.

The slightly higher cationic charge dose efficiency for PDADMAC over chitosan that was observed also at pH 6 is more pronounced at pH 4. This appears to suggest that the effect of cationic charge addition that was found to be dominating in coagulation at pH 6 is reduced at pH 4, probably in favour of an increased effect of the differences in chemical composition of PDADMAC and chitosan.

Because of higher protonation of the amine groups of chitosan at pH 4 (resulting in higher charge density of the chitosan) the difference in charge densities between PDADMAC and chitosan is lower at pH 4 than at pH 6. This should suggest that the higher cationic charge dose efficiency observed for PDADMAC is not due to higher charge density of the polymer. A possible explanation could be related to some kind of hydrophobic interaction between uncharged portions of NOM and polyelectrolyte. As pH is reduced a higher portion of the NOM is rendered uncharged and therefore more amenable to hydrophobic interaction. On the other hand the backbone of PDADMAC, containing a majority of $-CH_2-$ groups would be expected to be less polar, and therefore more amenable to hydrophobic interactions than chitosan which backbone consists of more polar -CHOH- groups.

The results do not offer concluding evidence to support such a hypothesis, but it could explain the higher cationic charge efficiency of PDADMAC over chitosan, and why this is more pronounced at a lower pH. Furthermore, these results appear to suggest that there may exist different mechanisms for the interaction between NOM and cationic polyelectrolytes, and that the relative importance of these depend on pH and the charge density of the NOM. However, it must be stressed that the results obtained with chitosan were somewhat controversial and in need of verification by further experiments. Accordingly further experiments are required before drawing conclusions from the discussion presented above.

Flocculation properties of NOM-polymer aggregates have been assessed based on observed removals after filtration through 11 μm paper filter as presented in figure 5.16 below.

Figure 5.16 shows a higher maximum removal of colour after filtration through 11 μm is with PDADMAC as coagulant than with chitosan. Taking into account the higher aggregate formation exhibited by PDADMAC at this dosage, this appears to be in agreement with basic flocculation theory (flocculation rate depending on concentration of primary particles). Highest observed removals (as well as residual turbidity) as function of specific polymer dose are found at approximately the same dose for both polymers.

Focusing on the right part of figure 5.16 it is seen that maximum removal is obtained at approximately the same cationic charge dose for PDADMAC and chitosan. The reason for the fact that maxima occur at approximately the same dosage both with respect to actual polymer dose and cationic charge dose is probably that the difference in stoichiometric charge densities between PDADMAC and chitosan is smaller at pH 4 (6,2 meq/g and 5,6 respectively) than at pH 6 (6,2 and .4,5 meq/g respectively).

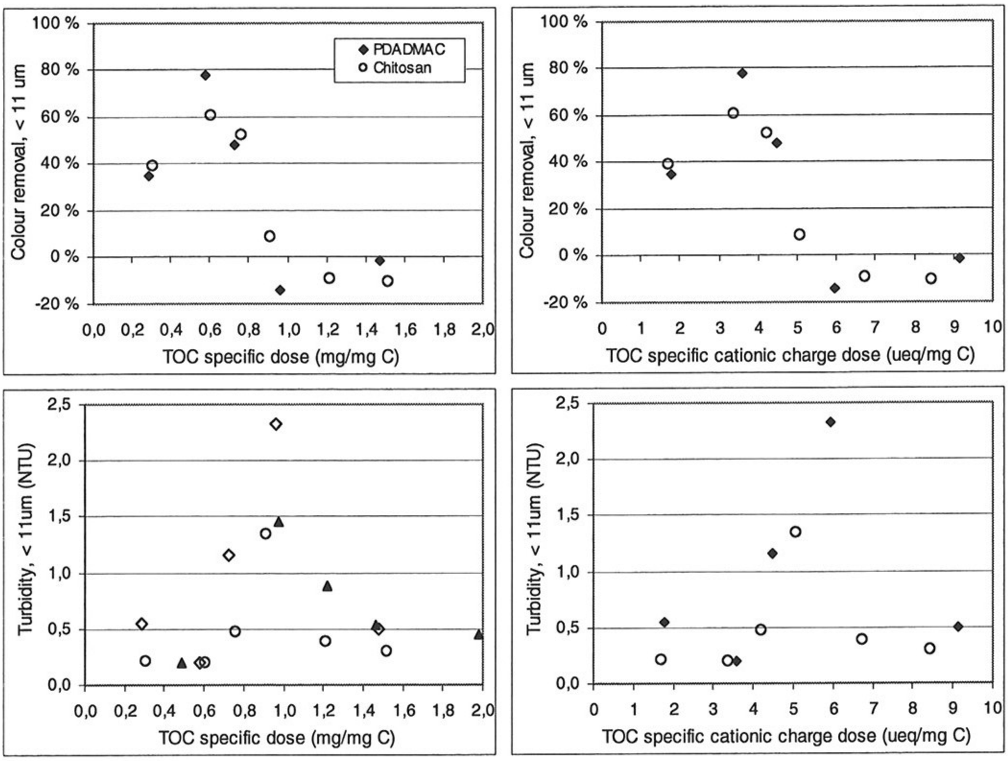


Figure 5.16. Comparison of flocculation properties of aggregates formed by coagulation of NOM with PDADMAC and with chitosan (F_A=0,05) at pH 4. Presented as residual turbidity and removals of colour after final filtration through 11μm pore size paper filter as function of TOC specific polymer dose (left) and TOC specific cationic charge dose (right).

5.2.4 Main findings on the effect of pH on coagulation and flocculation

- The results obtained with PDADMAC were in support of hypothesis E-1 stated in chapter 3: *Due to increased protonation of the carboxyl groups, and thus reduced anionic charge density, of the humic substances, lowering of pH from 6 to 4 results in improved dose efficiencies with respect to coagulation of NOM with cationic polyelectrolytes.* The results obtained with chitosan showed hardly any effect of lowering pH from 6 to 4 on coagulation of NOM and were therefore not in support of hypothesis E-1.

- With PDADMAC the highest observed removal after filtration through 0,1 µm decreased slightly (from about 95% to about 90%) with respect to colour, and more substantially (from about 58% to about 39%) with respect to dissolved TOC. The point of optimal dosage (with respect to maximum colour removal) shifts substantially downwards, from approximately 2,2 to 0,9 mg/mg TOC. It was suggested that a fraction of the NOM is rendered more or less deionised (due to protonation of carboxylic groups) as pH is reduced and that the neutralised fraction of NOM is incapable to interact electrostatically with the cationically charged polyelectrolyte.

- The results obtained with chitosan compared to those with PDADMAC did not support hypothesis E-2 stated in chapter 3: *With chitosan a reduction of pH will also result in a gain in cationic charge density due to protonation of the amine groups. Therefore the effect of reducing pH on polymer dose efficiency will be more pronounced for a weak polycation such as chitosan than for a strong polycation such as PDADMAC.*

- It was concluded that further experiments should be performed before drawing final conclusions with respect to the effect of pH on coagulation of NOM with chitosan.

- Comparison of results for chitosan and PDADMAC with respect to cationic charge dosage suggested that the effect of charge addition that was dominating at pH 6, was less pronounced at pH 4. However, due to the somewhat controversial finding with respect to chitosan it was stressed that further experiments are required before drawing conclusions on this issue.

5.3 Effect of the degree of acetylation in chitosans

In accordance with the hypotheses (B and C) stated in sub chapter 3.1 regarding the effect of polyelectrolyte charge density relative to the effect of chemical composition as such, it was expected that the efficiency of chitosans as coagulants for dissolved organic substances increases with decreasing degree of acetylation (F_A), and thus increasing charge density.

In order to directly assess the effect of degree of acetylation in chitosans in coagulation of NOM results from experiments performed at pH 6 and at pH 4 are presented as removals of colour and TOC after filtration through 0,1 μm membrane filter as function of TOC specific polymer dose as well as specific cationic charge dose in figure 5.17 below.

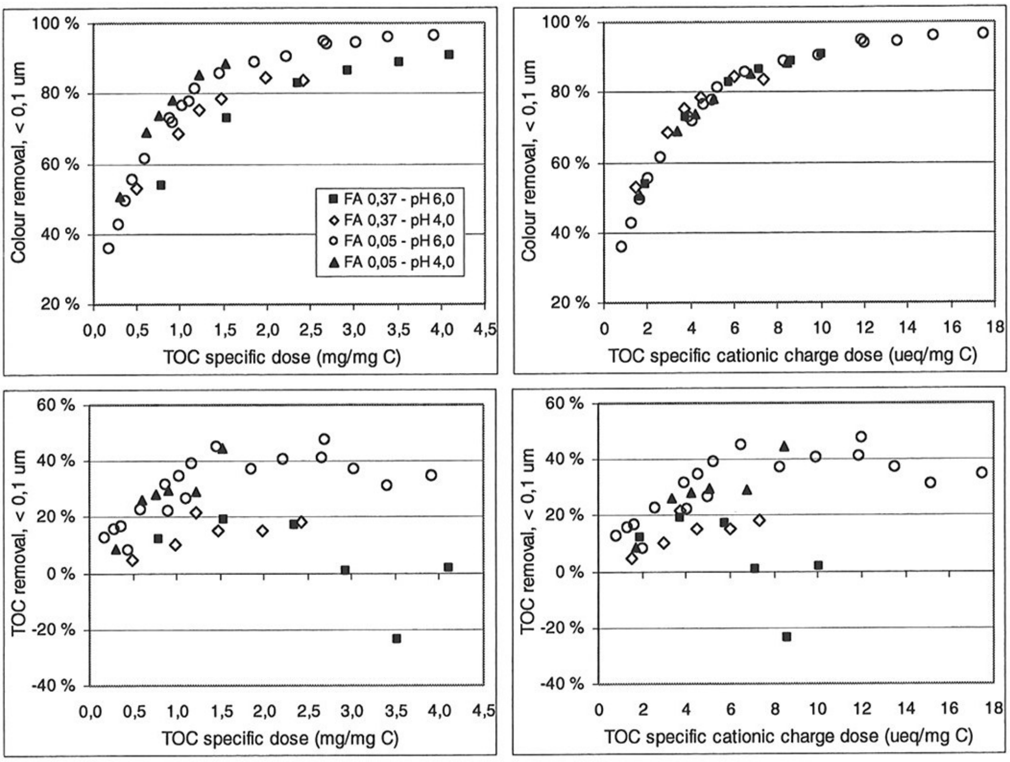


Figure 5.17. Effects of pH and degree of acetylation on coagulation of NOM with chitosan. Monitored as removal of colour and TOC after final filtration through 0,1 μm. Left: Removals as function of TOC specific polymer dose. Right: Removals as function of TOC specific cationic charge dose.

The upper left part of figure 5.17 shows that the chitosan with the lowest degree of acetylation (F_A 0,05), and therefore the highest cationic charge density, exhibits higher polymer dose efficiency with respect to coagulation of humic substances at both pHs. When the results are plotted as function of added cationic charge equivalents (upper right part of figure 5.17) the differences in dose efficiency both between the two chitosans and between the two coagulation pHs are more or less eliminated. It appears that the effect of degree of acetylation on coagulation of humic substances with chitosan is mainly related to the difference in charge densities that follows the degree of acetylation, and more specifically to the amount of cationic charge equivalents added. The results therefore seem to be in support of hypotheses B and C, as stated in the introduction to this sub chapter.

Considering the effect of pH on coagulation with the more highly acetylated chitosan ($F_A = 0,37$), it is noticeable that the results are more in accordance with the results obtained with PDADMAC. Lowering pH from 6 to 4 results in a significant increase in polymer dose efficiency. Furthermore it appears that an optimal dosage point (with respect to maximum coagulation) has been reached at pH 4.

5.4 Combined use of metal salt (iron chloride sulphate) and cationic polyelectrolyte coagulants

The purpose of the experiments reported in this chapter has been to test whether coagulation and flocculation could be improved by the combined use of a metal salt and a cationic polyelectrolyte. The design of the experiments included the testing of two different polyelectrolytes in combination with iron chloride sulphate at two different raw water pHs. This was done in order to enable a relative comparison of the effects of metal salt and polymer as co-coagulants at low dosages of both and to investigate the effect of pH in these systems. One strong (PDADMAC) and one weak (chitosan) polycation were selected for the tests in order to examine possible differences in polymer-metal salt – NOM interactions between a strong and a weak cationic polyelectrolyte.

In sub chapter 3.1 hypothesis F was stated on basis of the literature study:

F Combination of metal salt and cationic polyelectrolytes as coagulants for dissolved organic substances

> The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.

Coagulation of NOM in humic water with cationic polyelectrolytes and metal salt in combination was tested for PDADMAC and chitosan (F_A 0,05) in combination with iron chloride sulphate (JKL). The experiments were designed as two 2^3 factorial designs (one per polyelectrolyte) with two levels of polyelectrolyte dosage (1 and 2 mg/l) and iron chloride sulphate dosages (1 and 2 mg Fe/l) and raw water pH (5 and 6). Due to the acidity of iron chloride sulphate the actual coagulation pHs measured in samples of coagulated water were 4,8 and 5,9, respectively. Each combination was tested with one replicate. In addition the centre point (1,5 mg polymer/l - 1,5 mg Fe/l – pH 5,5) was tested with three replicates in order to obtain estimates of experimental error for significance testing using analysis of variance (ANOVA). Test designs and analysis of results were performed using commercially available software for statistical analysis (The Unscrambler v.7.5, CAMO ASA, Oslo).

The results from the experiments were interpreted by investigation of graphical presentations as well as statistically (significance testing).

5.4.1 Combination of PDADMAC and iron chloride sulphate

The results from coagulation of NOM with combined low dosages of PDADMAC and iron chloride sulphate are presented in figure 5.18 (below) as removals of colour and TOC after filtration through 0,1 µm membrane filter. Results from previous experiments with PDADMAC as sole coagulant at pH 6 and 4 have been included in the presentations in order to illustrate the effects of adding iron chloride sulphate as a co-coagulant.

Visual interpretation of the results presented in the upper part of figure 5.18 reveals a rather convincing indication that good coagulation of NOM can be achieved (75% colour removal and 40 % TOC removal after filtration through 0,1 µm membrane filter) using a low dosage of PDADMAC (2 mg/l) in combination with a low dosage of iron chloride sulphate (2 mg/l).

In the statistical analysis only one effect was found to be significant at the 95 % probability level (table 5-1, below). Increasing polymer dose from 1 to 2 mg/l increased coagulation efficiency measured as removal of colour after filtration through 0,1 µm membrane filter. Figure 5.18 (upper left) indicates a strong effect of increasing iron chloride sulphate dosage as well, but the error bars included for the 1 mg Fe/l – pH 5 series in figure 5.18 illustrates quite well why this effect was not found to be statistically significant. Experimental error estimated on basis of the results from three centre points in the experimental design is too high relative to the magnitude of the effects.

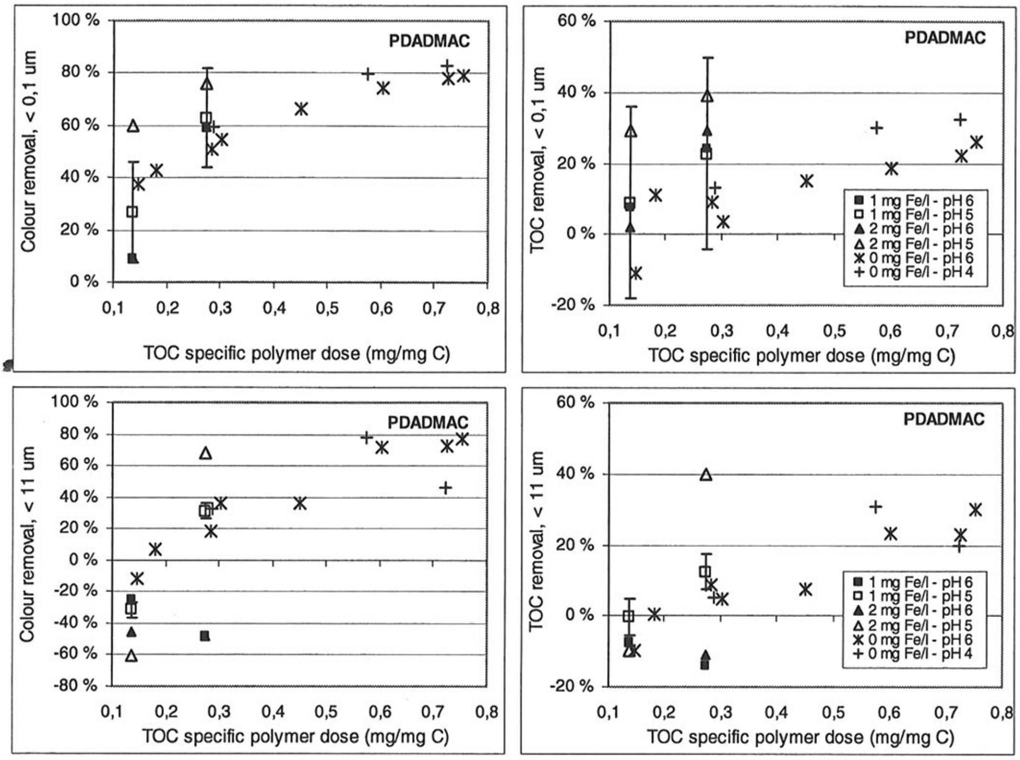


Figure 5.18. Coagulation and flocculation of NOM in humic water using iron chloride sulphate and cationic polyelectrolyte PDADMAC in combination. **Top:** Removal of TOC (right) and colour (left) after final filtration through 0,1 μm as function of TOC specific polymer dose and absolute iron chloride sulphate dose (as mg Fe/l) at two different pH's. **Bottom:** Removal of TOC (right) and colour (left) after final filtration through 11μm pore size paper filter as function of TOC specific polymer dose and absolute iron chloride sulphate dose (as mg Fe/l). Results from experiments using only PDADMAC are included for comparison. Error bars indicate experimental uncertainty of individual data points estimated on basis of three replicates of centre points in the factorial design and as described in chapter 4.6.

Focusing on the lower part of figure 5.18, the most striking feature is that acceptable flocculation properties of the aggregates are only observed for experiments with raw water pH 5 (filled symbols). This is probably due to the fact that iron chloride sulphate is substantially less efficient as a coagulant at pH 6 than at pH 5, and that the humic material carries a higher anionic charge density at pH 6 than at pH 5.

At pH 5 increasing coagulant dosages has a positive effect on removals after filtration through 11 μm paper filter. Especially increasing iron chloride dosage from 1 to 2 mg Fe/l in combination with 2 mg/l PDADMAC gives a substantial increase in removals relative to using PDADMAC as sole coagulant. At pH 6 increased coagulant dosages appear to have negative, or at best no, effects on the flocculation properties. And adding low dosages (1-2 mg Fe/l) of iron chloride sulphate at raw water pH 6 consequently gives poorer aggregate flocculation properties than the sole use of polyelectrolyte as coagulant.

A summary from the significance testing of the results from the experiments with combined use of PDADMAC and iron chloride sulphate as coagulants at pH 5 and 6 are presented in table 5.1 below.

Table 5-1. Results from significance testing on experiments with combined use of PDADMAC and iron chloride sulphate as coagulants at pH 5 and 6.

Variable	**Significant effects** at 95% probability (+ = positive, - = negative, ? = insignificant)			
	Colour removal (< 0,1 μm)	**TOC** removal (< 0,1 μm)	**Colour** removal (< 11 μm)	**TOC** removal (< 11 μm)
PDADMAC (1 mg/l → 2 mg/l)	+	?	+	+
Iron chloride sulphate (1 mg Fe/l → 2 mg Fe/l)	?	?	?	?
pH (5 → 6)	?	?	-	-

Results from experiments with PDADMAC as sole coagulant included in figure 5.18 for comparison shows that in order to achieve the same coagulation with PDADMAC alone dosages of at least 5-6 mg/l (recalculated from TOC specific dosages) would be required. With iron chloride sulphate as sole coagulant (reported in chapter 5.1.2) removals of colour and TOC after filtration through 0,1 μm membrane filter of 75% and 40 % respectively could be obtained at dosages of approximately 3 mg Fe/l (at pH 4,5-5,5). However, in order to also get acceptable flocculation a dosage of 7 to 10 mg Fe/l was required when using only iron chloride sulphate (again at pH 4,5 –5,5).

To conclude, the results with PDADMAC and iron chloride sulphate in combination seem to be in support of the hypothesis (F) with respect to removal of colour: *The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.*

5.4.2 Combination of chitosan ($F_A = 0{,}05$) and iron chloride sulphate

The results from coagulation of NOM with combined low dosages of chitosan ($F_A = 0{,}05$) and iron chloride sulphate are presented in figure 5.19 (below) as removals of colour and TOC after filtration through 0,1 μm membrane filter. Results from previous experiments with chitosan as sole coagulant at pH 6 and 4 have been included in the presentations in order to illustrate the effects of adding iron chloride sulphate as a co-coagulant.

A summary from the significance testing of the results from the experiments with combined use of chitosan and iron chloride sulphate as coagulants at pH 5 and 6 are presented in table 5.2 below.

Table 5-2. Results from significance testing on experiments with combined use of PDADMAC and iron chloride sulphate as coagulants at pH 5 and 6.

Variable	**Significant effects** at 95% probability (+ = positive, - = negative, ? = insignificant)			
	Colour removal (< 0,1 μm)	**TOC** removal (< 0,1 μm)	**Colour** removal (< 11 μm)	**TOC** removal (< 11 μm)
Chitosan (1 mg/l → 2 mg/l)	+	+	+	?
Iron chloride sulphate (1 mg Fe/l → 2 mg Fe/l)	?	+	-	+
pH (5 → 6)	-	-	-	-

Figure 5.19 (upper part) demonstrates that good coagulation (up to respectively 70 and 35% for colour and TOC) can be achieved by combining a low dose (2 mg/l) of chitosan with a low dose (2 mg Fe/l) of iron chloride sulphate. As with PDADMAC, the lower part of figure 5.19 shows that acceptable flocculation properties of the aggregates are only observed for experiments with raw water pH 5 (filled symbols).

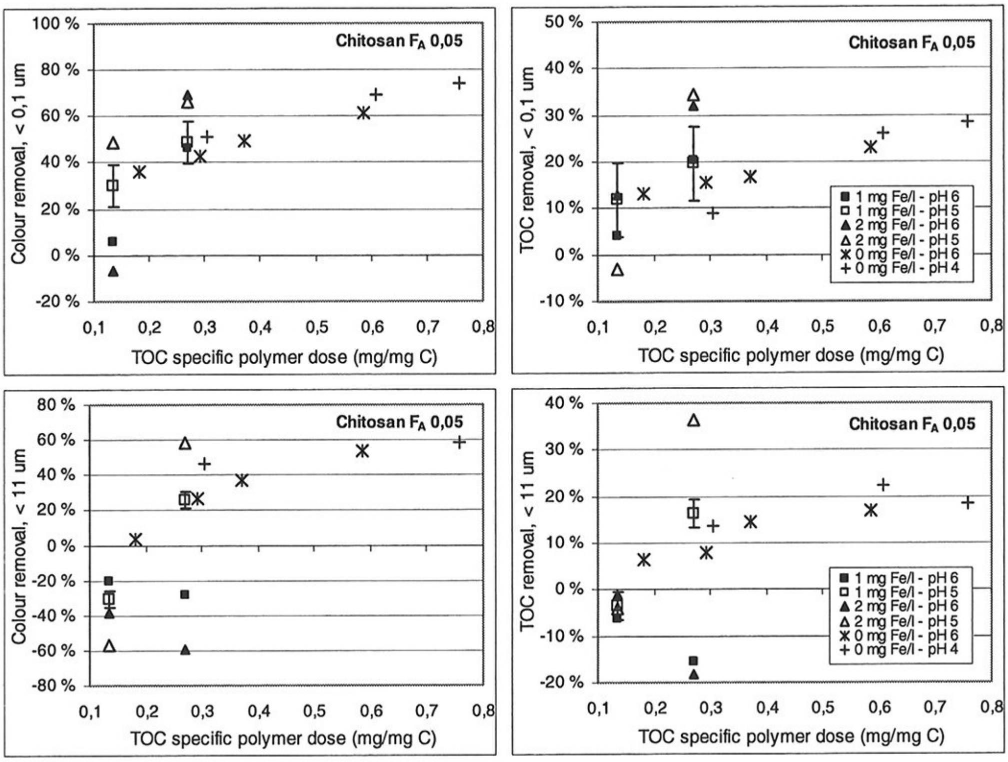


Figure 5.19. Coagulation of NOM in humic water using iron chloride sulphate and cationic polyelectrolyte chitosan F$_A$ 0,05 in combination. Presented as removal of TOC and colour after final filtration through 0,1 μm as function of TOC specific polymer dose and absolute iron chloride sulphate dose (as mg Fe/l) at two different pH's. Results from experiments using only chitosan are included for comparison. Error bars indicate experimental uncertainty of individual data points estimated on basis of three replicates of centre points in the factorial design and as described in chapter 6.1.1.

Results from experiments with chitosan as sole coagulant included in figure 5.19 for comparison shows that in order to achieve the same coagulation with chitosan alone dosages of at least 5-6 mg/l (recalculated from TOC specific dosages) would be required. With iron chloride sulphate as sole coagulant (reported in chapter 5.1.2) removals of colour and TOC after filtration through

0,1 μm membrane filter of 75% and 40 % respectively could be obtained at dosages of approximately 3 mg Fe/l (at pH 4,5-5,5). However, in order to also get acceptable flocculation a dosage of 7 to 10 mg Fe/l was required when using only iron chloride sulphate (again at pH 4,5 –5,5).

To conclude, the results with chitosan and iron chloride sulphate in combination seem to be in support of the hypothesis (F) with respect to removal of colour: *The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.*

Comparing the results obtained with PDADMAC and chitosan, there appears to be no indications that the strong polycation PDADMAC performs principally different from the weak polycation chitosan in combination with a metal salt coagulant.

5.4.3 Main findings on combined use of metal salt and cationic polyelectrolyte coagulants

- The results showed that a high degree of coagulation of coloured NOM (75 and 70% for PDADMAC and chitosan respectively) could be achieved by combining a low dosage (2 mg/l) of cationic polyelectrolyte with a low dosage (2 mg Fe/l) of iron chloride sulphate. However, good flocculation properties (measured as removal after filtration through 11 μm paper filter) were only observed with at pH 5, and not at pH 6, at these dosages

- The results appeared to be in support of hypothesis F stated in sub chapter 3.1: *The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.*

- The results gave no indications that a strong polycation (PDADMAC) performs principally different from a weak polycation (chitosan) in a low dosage combined polyelectrolyte – metal salt coagulant system.

6 RESULTS AND DISCUSSION ON COAGULATION AND FLOCCULATION OF ORGANIC SUBSTANCES IN WASTEWATER (MOVING BED BIOFILM REACTOR EFFLUENT)

The main intention in including coagulation experiments on wastewater was to investigate the interaction of different cationic polyelectrolytes with different kinds of dissolved organic substances and under different conditions. More specifically the objective was to investigate how the same polymers used in the humic water study would interact with humic as well as non-humic dissolved organic substances in a more heterogeneous and particle rich water. Analogue to the study on NOM the following sub objectives were formulated:

- By choice of experimental methodology, to study the coagulation process (of dissolved organic substances) as such, disconnecting the obtained results from dependency on floc growth and separability of formed flocs
- To compare coagulation efficiency and performance of a wide spectrum of different cationic polyelectrolyte coagulants, over a broad dosage range (regardless of economical concerns), ranging from sub optimal dose to overdosage (if obtainable)
- To compare the dosage responses with respect to coagulation of dissolved organic matter with the formation of flocs separable by filtration through 11 μm
- To compare coagulation dosage response of UV-absorbing dissolved organic matter relative to the bulk of the dissolved organic matter measured as COD and TOC

The main objective in the choice of polymers for testing was again to cover a wide spectre of different cationic polyelectrolyte coagulants, with emphasis on cationic and coagulant and especially to investigate the effect of polyelectrolyte chemical composition and charge density relative to the effect of the mere addition of cationic charge equivalents. Furthermore it was of special interest to examine the performance of chitosan relative to synthetic polymers.

As mentioned in the literature study, sub chapter 2.6, although a few investigators have observed and commented on the coagulation of dissolved organic matter as a side effect to the coagulation and flocculation of particles, no references were found specifically addressing the coagulation of dissolved organic matter in wastewater with organic polymers. This made it more difficult to formulate hypotheses with respect to the coagulation of dissolved organic substances in wastewater by polyelectrolytes. However it was stated, as hypothesis G on the relationship between polyelectrolyte coagulation of dissolved organic substances in humic water and wastewater that:

> *A significant portion of the dissolved organic substances in wastewater is made up of humic-like substances and the coagulation of these by polyelectrolytes can be explained accordingly to that of humic substances in surface water*

This means that some of the hypotheses (B, C and F) originally formulated with respect to the coagulation of dissolved NOM in humic water also were of interest with respect to the experiments on wastewater:

B Differences in the polyelectrolytes efficiencies as coagulants for dissolved organic substances

Differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain

C The nature of the effect of polyelectrolyte charge density on coagulation of dissolved organic substances

With respect to coagulation of dissolved humic substances the effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such.

F Combination of metal salt and cationic polyelectrolytes as coagulants for dissolved organic substances

The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.

6.1 Coagulation of dissolved organic substances at pH 6,0

6.1.1 Comparison of coagulation dosage response of the different polyelectrolytes

Analogous to the treatment on coagulation of humic water dissolved is here defined operationally as substances passing though a 0,1 μm membrane filter, regardless of whether the substances are truly dissolved in a thermodynamic understanding of the word. Accordingly, coagulation is defined operationally as the formation of aggregates that are withheld in a 0,1 μm membrane filter and thus observable as the removal of COD, UVA or TOC relative to the raw water after a final filtration through a 0,1 μm pore size membrane filter.

Unlike for humic water these experiments have not been performed on reproducible raw water. On the contrary the raw water showed (as expected) broad variation in composition as well as concentration. Therefore the results obtained with each raw water batch have to be investigated separately. Descriptions of the raw waters used in these experiments are given in chapter 4. However, for the sake of convenience, a short summary is presented below:

Coagulation experiments on wastewater were performed on effluent water from a highly loaded lab scale moving bed biofilmreactor (MBBR) fed with municipal wastewater from a nearby residential area. The MBBR was operated at very high loading rate (15 min detention time) as part a contract project at SINTEF (Melin *et al*, 2002) investigating a treatment process for wastewater.
The process combines a biofilm process with coagulation and dissolved air flotation using combinations of metal salt and polyelectrolyte coagulants and is presented schematically in figure 4.2, chapter 4.

Raw water composition was as presented in table 6-1 below.

Table 6-1. Composition of unfiltered biofilmreactor effluent (used as raw water in coagulation experiments). Dissolved is defined as substances passing a 0,1 μm membrane filter.

Parameter	08.11.01	05.12.01
pH (adjusted)	6,0	6,0
Turbidity (NTU)	43	91
Suspended solids (mg/l)	-	180
Total COD (mg O/l)	123	272
Turbidity < 11 μm (NTU)	5,5	6,6
Dissolved COD (mg O/l)	46	55
Dissolved UVA (m-1)	36	38
Dissolved TOC (mg C/l)	17	21

Results with respect to coagulation of dissolved organic substances, measured as removal of COD after filtration through 0,1 μm membrane filter, is presented graphically in figure 6.1 below.

Figure 6.1 shows that 30-35% and 20-25% removal (respectively for experiments performed on 08.11.01 and 05.12.01) of dissolved organic matter measured as COD < 0,1 μm is achieved with all the cationic polyelectrolytes tested. Required dosages in order to obtain maximal coagulation are in the ranges 18-30 mg/l and 15-20 mg/l respectively. The error bars indicating the analytical uncertainty of the COD-analysis together with the distribution of the dosage response points show that discriminations between the performances of the different polyelectrolytes would be questionable. It is however noticeable that chitosan is the only polyelectrolyte exhibiting signs of overdosage (in series 08.11.01).

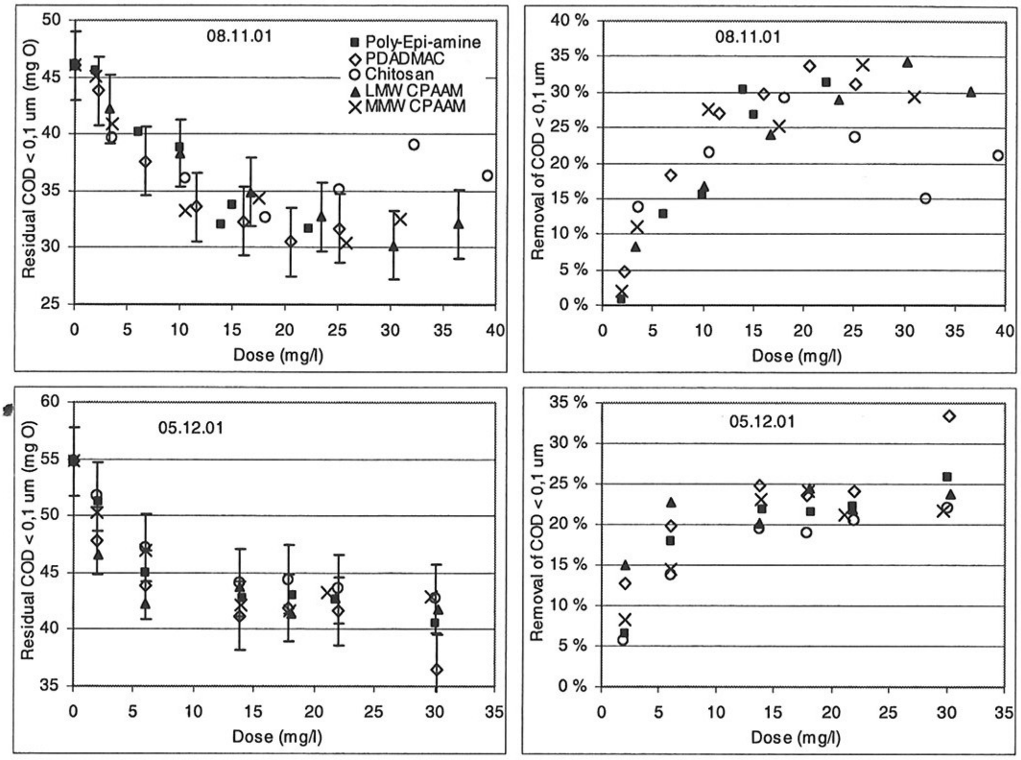


Figure 6.1. Comparison of coagulation of dissolved organic substances in wastewater by cationic polyelectrolytes monitored as residual and relative removal of COD after final filtration through 0,1 μm membrane filter. **Top:** Experiments performed 08.11.01. **Bottom**: Experiments performed 05.12.01. **Error bars** indicate 95 % confidence interval of measured COD value (one measurement) based on analysis repeatability test performed on raw water (appendix B).

In order to relate coagulation of dissolved organic substances to flocculation of particulate matter and new-formed aggregates, turbidity was measured in sample aliquots having passed 11 μm paper filters. These results are presented in figure 6.2 below. In order to show the difference in performance between chitosan and the synthetic polyelectrolytes more clearly, the latter are represented by PDADMAC. Results for all polyelectrolytes tested are presented graphically in appendix D.

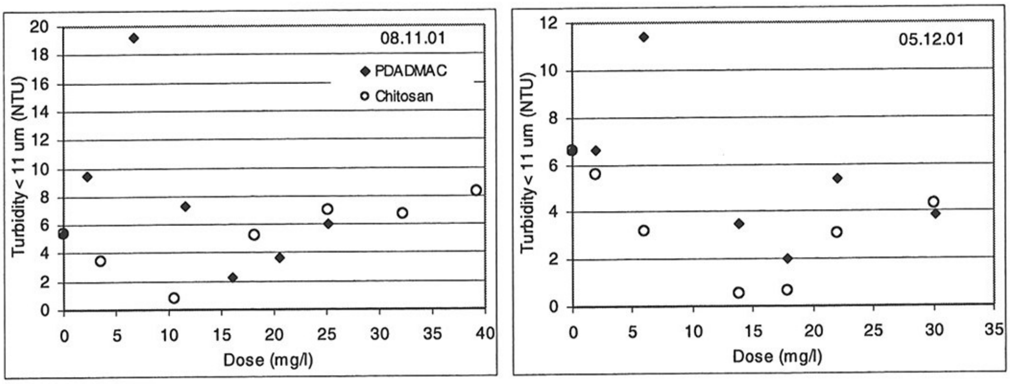


Figure 6.2. Residual turbidity after coagulation and filtration through 11 µm paper filter as function of polymer dose for experiments performed on 08.11.01 and 05.12.01.

Comparisons of the dose responses of coagulation and removal after filtration through 0,1 µm in figure 6.1 and dose responses with respect to residual turbidity after filtration through 11 µm paper filter show that for the synthetic polycations tested the formation of aggregates coincides with a net formation of turbidity. Furthermore it can be observed that the dosages at which net removals of turbidity are achieved coincide with the flattening out of the curves for removal of dissolved COD in figure 6.1. In other words, the results seem to indicate that, with the synthetic polyelectrolytes tested, acceptable flocculation of particles and new-formed aggregates first takes place after all coagulable dissolved organic matter has been coagulated. This appears to be consistent with the findings of Narkis and Rebhun (1996) as referred in chapter 2.6.2.

The most noticeable and interesting feature of figure 6.1 is however the results obtained with chitosan. Although giving rise to approximately the same degree of coagulation of dissolved COD, no accompanying increase in residual turbidity (after filtration through 11 µm paper filter) is observed with chitosan. It appears that chitosan is more capable of acting both as a coagulant and a flocculant than the synthetic polyelectrolytes at low dosages. This aspect will be revisited in chapter 6.3.

6.1.2 Comparison of dosage responses with respect to UVA, COD and TOC

Examples of coagulation dosage responses for UV-absorbing dissolved organic matter relative to the bulk of the dissolved organic matter measured as COD and TOC are presented graphically in figure 6.3 below.

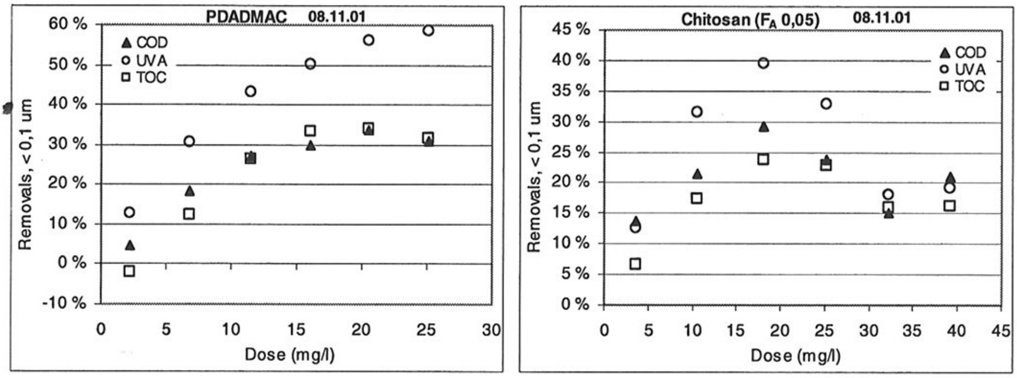


Figure 6.3. Comparison of relative removals of UV-absorbing substances (UVA, m^{-1}), total organic carbon (TOC, mg C/l) and chemical oxygen demand (COD, mg O/l) from wastewater after coagulation, flocculation and final filtration through 0,1μm. membrane filter.

The dosage response observed for PDADMAC in the left part of figure 6.3 is representative for the response of all tested polycations on both occasions (08.11.01. and 05.12.01) except for that of chitosan in the experiments performed 08.11.01 (right part of figure 6.3). A full graphical presentation of these results is given in appendix D.

Focusing first on the typical response as exemplified by PDADMAC, figure 6.3 shows that the relative removal of UV-absorbing substances is generally substantially higher than removals of the bulk of dissolved organic substances, measured as COD or TOC. Actually, the ratios of UVA-removals relative to TOC-removals appear to be quite comparable to those observed in the case of humic water (sub chapter 5.1.3.2). This seems to indicate that in wastewater as in humic water, the humic-like material is more susceptible to coagulation by polymers than the bulk of the dissolved organic matter. It is also interesting to notice that the coagulation of UV-absorbing substances appears to continue to increase with polymer dosage after the dose-response with respect to coagulation of bulk dissolved organic substances (measured as removal of COD and TOC) flattens out. In chapter 5 it was shown that the interaction between humic substances and cationic polyelectrolytes in humic water at pH 6 was predominantly explained by the addition of cationic charge equivalents to the water. The phenomena commented on above could, in this line of reasoning, be explained by a higher demand for cation charge dosage, before maximum coagulation is achieved, for humic like substances in wastewater than for non-humic material.

The results with chitosan on 08.11.01 presented in the right part of figure 6.3 are atypical in the sense that overdosage is observed, but they show similar dosage responses for all parameters, all exhibiting maximal removal at the same dosage.

6.1.3 Effect of differences in raw water COD concentrations and distributions

The size distributions with respect to COD of the raw waters used in experiments performed on 08.11.01 and 05.12.01 are presented in chapter 4.4.2. The distributions show that the concentrations of COD in size fractions 1,2 - 11 μm, 0,1 - 1,2 μm and < 0,1 μm are respectively 60%, 130% and 20% higher in raw water 05.12.01 than 08.11.01. The total COD concentration in raw water 05.12.01 is more than twice that of raw water from 08.11.01. With respect to COD content in size fractions larger than 11 μm, the raw water of 05.12.01 contains three times more COD than the raw water of 08.11.01 (196 and 65 mg O/l respectively). The experiments on humic water demonstrated an expected concentration-dose stoichiometry for the coagulation of dissolved NOM. A similar concentration-dose stoichiometry would be expected in experiments with wastewater, but in this case interactions between polyelectrolytes and a heterogenic population of particle surfaces would also have to be taken into account. It is reasonable to assume that adsorption of polyelectrolyte to these surfaces will occur and that this adsorption may be in competition with polyelectrolyte interaction with dissolved organic matter.

An attempt to investigate this has been made by plotting absolute removals of dissolved COD (COD < 0,1 μm) as function of polymer dose from experiments performed on 08.11.01 and 05.12.01 in the same graphs in figure 6.4 below. The experiments with PDADMAC and chitosan are chosen as examples because they are typical of the two different responses that are observed. Plots for poly-Epi-amine and LMW CPAAM show principally the same picture as that for PDADMAC whereas MMW CPAAM shows principally the same behaviour as chitosan (appendix D).

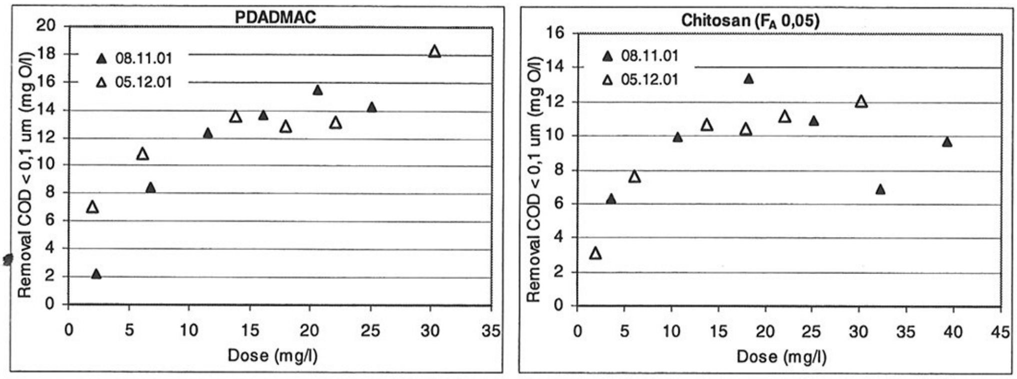


Figure 6.4. Absolute removals of dissolved COD as functions of polymer doses in coagulation experiments on wastewater with PDADMAC and chitosan. Results from experiments conducted 08.11.01 and 05.12.01 are plotted in the same graphs in order to reveal possible simple concentration – dose stoichiometries.

As long as information about the charge density of the dissolved organic matter as well as of the particle surfaces (organic as well as inorganic) are not obtained and taken into account, the results presented in figure 6.4 must be interpreted with caution.

If one were to assume that a rough stoichiometry between COD-concentration (total or individual fractions) and needed polymer dose in order to coagulate a certain amount of dissolved COD existed, one would expect to find a lower dose efficiency in the experiments performed on 05.12.01 than 08.11.01 as COD concentrations in the former are markedly higher than in the latter in all size fractions. This would reveal itself in figure 6.4 in that the data points of 05.12.01 would be shifted downwards with respect to removal at equal doses relative to the data points of 08.11.01. This is, however, not the case in figure 6.4. On the contrary, the dose efficiency with respect to coagulation of dissolved organic matter (COD < 0,1 μm) is at least as high in the experiments on raw water with a substantially higher total concentration (and concentrations in individual size fractions) of COD and particulate matter (05.12.01). At low doses of PDADMAC the observed absolute dose efficiency is even higher at higher total concentrations of COD.

The results in figure 6.4 appear to indicate that the presence of particle surfaces and adsorption of polyelectrolyte to these surfaces does not negatively affect the coagulation of dissolved organic matter with polyelectrolyte. Rather, there appears to be indications (PDADMAC) that the presence of particulate matter might even have a positive effect on the polymer dose efficiency in coagulation of dissolved organic matter. This is considered to be an important finding and it would be of great interest to follow it up with further experiments.

As reported in sub chapter of the literature study, several investigators have found that the presence or addition of mineral particles in humic waters has a positive effect on the removal of humic substances by coagulation with cationic polyelectrolytes. Amy and Chadik (1983) suggested that the particles provided nuclei for floc formation. With respect to coagulation, measured as removal of dissolved substances after filtration through 0,1 μm membrane filter, this line of reasoning would suggest that the aggregates formed are, at least partially, smaller than 0,1 μm, and that a certain degree of flocculation might be necessary to give aggregates separable at 0,1 μm. Under this assumption it could be conceivable that the flocculation of aggregates up to 0,1 μm size benefits from high concentrations of particulate matter. This issue will be revisited in chapter 7, comparing coagulation of dissolved organic substances in wastewater and humic water.

6.1.4 Main findings on the coagulation of dissolved organic substances in wastewater

- 30-35% and 20-25% removal respectively (for experiments performed on 08.11.01 and 05.12.01) of dissolved organic matter measured as COD < 0,1 μm was achieved with all the cationic polyelectrolytes tested.

- The results with respect to dissolved COD or TOC gave no sound basis for distinguishing between the relative coagulation efficiencies of the different polyelectrolytes.

Comparisons of dosage response for coagulation of dissolved COD and for residual turbidity after filtration through 11 μm paper filter revealed principal differences in the performances of the synthetic (strong) polycations relative to that of the weak polycation chitosan. Whereas for the synthetic polycations the formation of aggregates at low dosages was accompanied by an increase in residual turbidity, chitosan showed net removal of turbidity even at low doses.

- With the synthetic polyelectrolytes the results seemed to indicate that acceptable flocculation of particles and new-formed aggregates first takes place after all coagulable dissolved organic matter has been coagulated.
- Chitosan appeared to be more capable of acting both as coagulant and flocculant than the synthetic polyelectrolytes at low dosages. This aspect will be revisited in chapter 6.3.

As was observed in coagulation of humic water, relative removals of UV-absorbing dissolved organic substances were in general substantially higher than removals of the bulk of dissolved organic substances, measured as COD or TOC. Removals with respect to TOC after filtration through 0,1 μm were comparable to those obtained for COD.

Plots of results from the experiments performed on the two different raw waters (08.11.01 and 05.12.01) in the same graph indicated that the presence of particle surfaces and adsorption of polyelectrolyte to these surfaces did not negatively affect, by competing for the polyelectrolyte molecules, the coagulation of dissolved organic matter with polyelectrolyte. Rather, there appeared to be a positive effect of the presence of particulate matter on the polymer dose efficiency in coagulation of dissolved organic matter.

6.2 Effect of polyelectrolyte charge density on coagulation of dissolved organic substances

Analogous with the results from coagulation of humic water, effects of polymer charge densities on the coagulation of dissolved organic substances have been investigate by recalculation of absolute polymer dosages to dosages of cationic charge equivalents and by plotting absolute removals of COD after final filtration through 0,1 μm membrane filter as functions of both (figure 6.5).

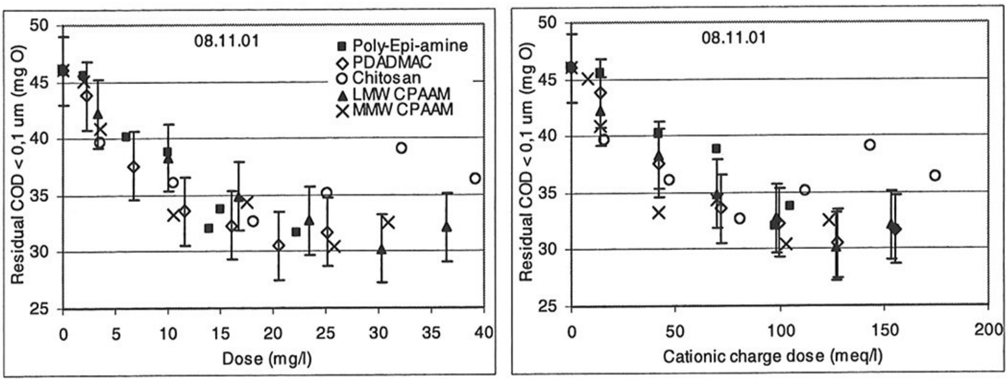


Figure 6.5. Comparison of coagulation of dissolved organic substances in wastewater with different cationic polymers measured as residual COD < 0,1 µm as function of polymer dose vs. cationic charge equivalents dose after coagulation and final filtration through 0,1 µm pore size membrane filter. **Left:** Residual COD < 0,1 µm as function of polymer dose (mg/l). **Right:** Residual COD < 0,1 µm as function of cationic charge dose (µeq/l). **Error bars** indicate 95 % confidence interval of measured COD value (one measurement) based on analysis repeatability test performed on raw water (appendix B).

The magnitude of uncertainty of the COD analysis makes interpretations of differences in polymer performances with respect to COD removal after final filtration through 0,1 µm difficult. Correspondingly it becomes difficult to draw conclusions on the effects of cationic charge densities of the polymers in figure 6.5. It appears, however, that the differences in polymer performances become smaller when plotted as function of cationic charge dose rather than absolute polymer dose.

The uncertainty in the analysis of dissolved UV-absorbing substances is much lower relatively to the measured values compared to dissolved COD (relative standard deviation of 1 % vs. 5 %). Therefore these results can more easily be interpreted with respect to the significance of polymer charge density in the coagulation of dissolved organic substances. Results from experiments performed on 08.11.01 and 05.12.01 are presented as residual dissolved UV-absorbing substances as function of absolute polymer dose and polymer dose as cationic charge equivalents in figure 6.6 below.

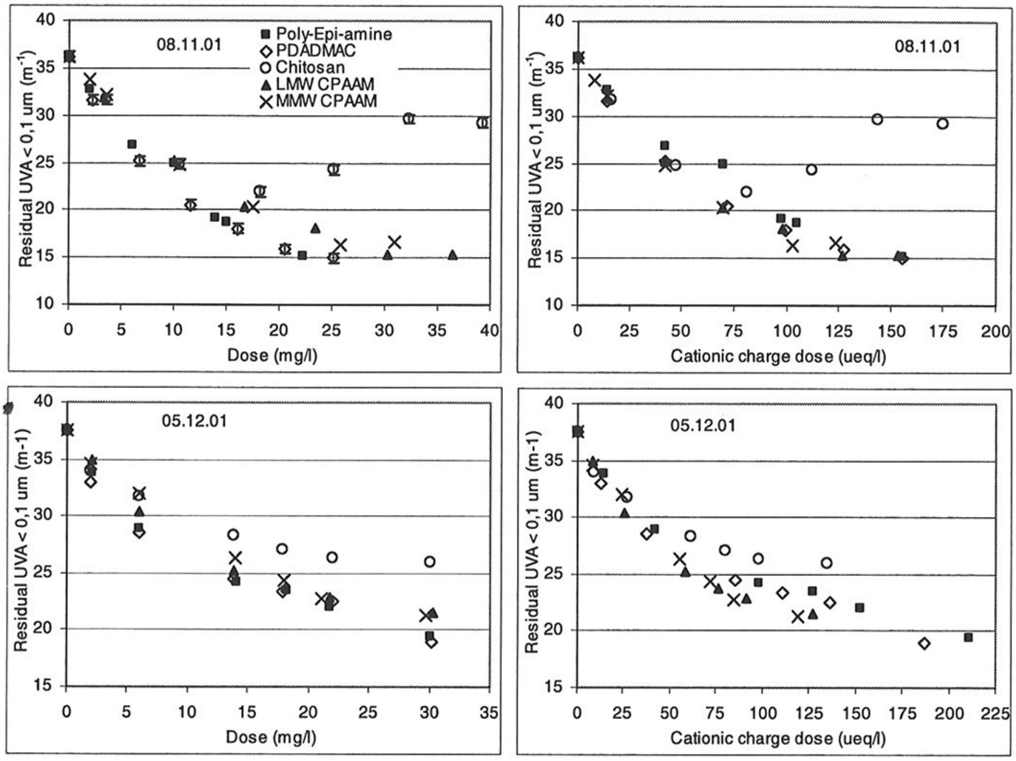


Figure 6.6. Comparison of coagulation of dissolved UV-absorbing substances in wastewater with different cationic polymers measured as residual COD < 0,1 μm as function of polymer dose vs. cationic charge equivalents dose after coagulation and final filtration through 0,1 μm pore size membrane filter. **Left:** Residual UVA < 0,1 μm as function of polymer dose (mg/l). **Right:** Residual UVA < 0,1 μm as function of cationic charge dose (μeq/l). **Error bars** (only included in top left graph) indicate 95 % confidence interval of measured UVA value (one measurement) based on analysis repeatability test performed on raw water (appendix B).

Results obtained 08.11.01 show a tendency similar to that observed in humic water. This is the raw water batch with the highest content of UV-absorbing, humic like organic substances relative to dissolved and total organic material measured as COD. Although not as clear as in the case of humic water, removal efficiencies appear to fall in two groups following the division in polymer charge density level. PDADMAC and Poly-Epi-amine, having significantly higher charge densities than the rest, show somewhat higher dose efficiencies than the others. The tendencies with respect to the effect of polymer charge density appear not to be reproduced in results obtained 05.12.01. The results do therefore not support any strong conclusions with respect to the effect of polymer charge densities on the coagulation of UV-absorbing dissolved organic substances in wastewater. However, when plotting the results from experiments performed 08.11.01 against cationic charge dosage rather than absolute polymer dose, this division or grouping is more or less cancelled out, indicating that at least in these experiments the differences in polymer dose efficiency observed may be attributed to the mere differences in cationic charge equivalents added. This might be considered to be in partial support of hypotheses B and C stated in sub chapter 3.1 and in the introduction to chapter 6.

6.3 Interaction of polyelectrolyte with different size fractions of COD

6.3.1 Flocculation monitored as removal after filtration through 11 μm paper filter

In chapter 6.1.1, comparisons of dosage response for coagulation of dissolved COD and for residual turbidity after filtration through 11 μm paper filter revealed principal differences in the performances of the synthetic (strong) polycations relative to that of the weak polycation chitosan. Whereas for the synthetic polycations the formation of aggregates at low dosages was accompanied by an increase in residual turbidity, chitosan showed net removal of turbidity even at low doses. A similar effect was observed in coagulation of humic raw water. Chitosan generally exhibited substantially lower turbidity formation than the synthetic, strong polyelectrolytes; especially at dosages necessary to obtain maximum coagulation of dissolved NOM.

An interesting question arises from the observed differences in turbidity formation. Could this divergence with respect to turbidity formation be caused by differences in the interaction of the polyelectrolytes with different size fractions, and possibly chemical fractions, of the organic matter? In order to investigate the parallel or combined interaction of polyelectrolytes with dissolved organic substances and particulate organic matter in the wastewater, samples of raw water as well as coagulated water were sequentially filtered through 11 μm, 1,2 μm and 0,1 μm filters and each aliquot analysed for COD.

One explanation of the substantial formation of turbidity observed with the synthetic, strong polyelectrolytes at low dosages could be some kind of preferential interaction with dissolved organic substances, at the expense of interaction with particulate matter, resulting in aggregates smaller than 11 μm.

If this is the case one would expect to observe a substantial build up of COD in size fractions smaller than 11 μm accompanying the formation of residual turbidity after filtration through 11 μm. Another explanation could be that all polyelectrolytes interact simultaneously with all charged surfaces, but that chitosan produces aggregates with dissolved organic substances that flocculate, or interact with particulate matter, more readily than aggregates formed by the synthetic polyelectrolytes, as was proposed for the coagulation of humic substances in experiments on humic water.

These questions are investigated in figures 6.7 and 6.8 below.

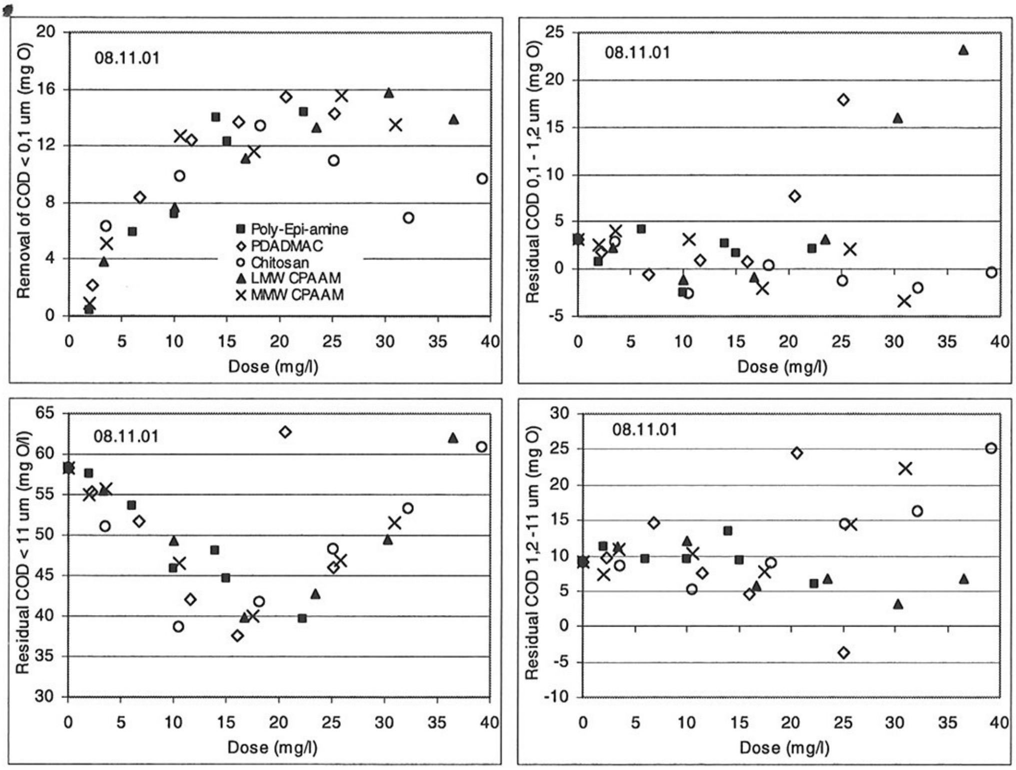


Figure 6.7. Removal of dissolved COD and residual COD within specific size fractions as functions of polymer dose. Experiment performed 08.11.01.

Figure 6.7 shows no indications of substantial build up of COD in the size fractions smaller than 11 μm. On the contrary, the lower left part of figure 6.7 shows that all polyelectrolytes cause some degree of flocculation of COD to floc sizes larger than 11 μm. The formation of aggregates smaller than 11 μm resulting in increased turbidity after filtration through 11 μm observed for synthetic polyelectrolytes therefore has to be balanced by the flocculation of particulate COD to form flocs separable by 11 µm filters.

In other words, the results do not seem to indicate that the synthetic polyelectrolytes interact preferentially with dissolved organic matter. Rather, the results presented in figure 6.7, together with results on residual turbidity after filtration through 11 µm (figure 6.2 and appendix D), appear to indicate that chitosan forms aggregates with dissolved organic matter that more readily flocculates, internally or with particulate matter, to size separable at 11 µm filter pore size. The same principal findings are observed in the experiments performed 05.12.01 presented in figure 6.8 below.

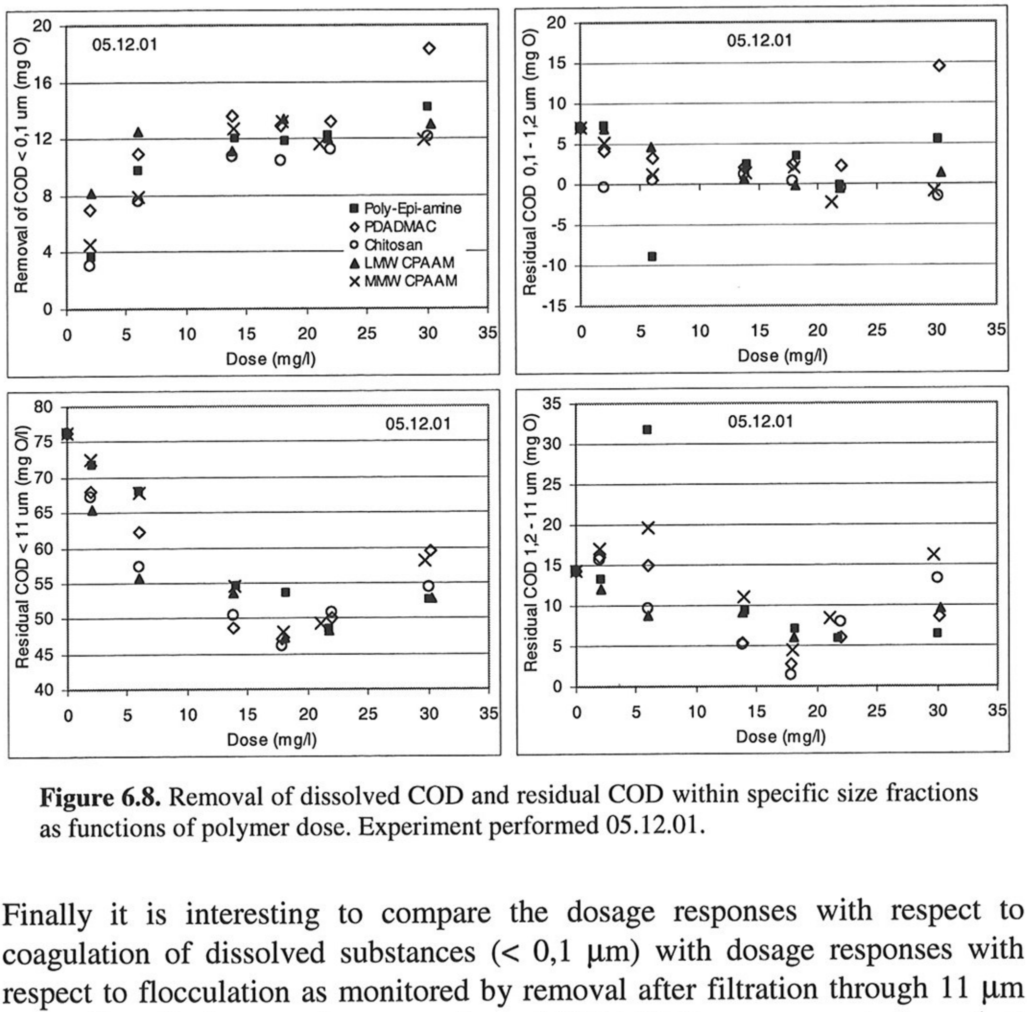


Figure 6.8. Removal of dissolved COD and residual COD within specific size fractions as functions of polymer dose. Experiment performed 05.12.01.

Finally it is interesting to compare the dosage responses with respect to coagulation of dissolved substances (< 0,1 µm) with dosage responses with respect to flocculation as monitored by removal after filtration through 11 µm paper filter. In the experiments performed 08.11.01 there appears to be a clear tendency for all polyelectrolytes tested except for the poly-Epi-amine that the optimal dose with respect to flocculation is substantially lower than the necessary dose to achieve highest observed coagulation of dissolved substances. This appears not to be the case in the experiments performed 05.12.01 where dosage optima with respect to coagulation of dissolved substances and flocculation more or less coincide.

6.3.2 Comparison with sedimentation

In order to compare removals obtained by filtration through paper filter (11 µm) after flocculation with sedimentation, all jars were submitted to settling (after sampling for filtration) in experiments performed on 05.12.01. Based on visual inspection of particle removal efficiency (clarity of supernatant), the three jars (dosages) per coagulant showing the best particle removal were sampled and submitted to analysis of residual turbidity, COD and suspended solids.

Results with respect to residual COD and turbidity after settling are presented together with corresponding results after filtration through 11 µm paper filter in figure 6.9.

Figure 6.9 (below) shows that although generally lower residual COD and turbidity is achieved after filtration through 11 µm relative to settling, optimal doses for filtration and settling correspond fairly well. Furthermore figure 6.9 appears to confirm that chitosan is more efficient in forming separable flocs than the synthetic polyelectrolytes, especially with respect to particle removal measured as turbidity (lower right part of figure 6.9). Results from suspended solids analysis after settling presented in figure 6.10 (below) confirms this finding.

Considering the ability to form flocs separable by filtration through 11 µm as presented in figure 6.9 (upper parts), there appears to be no clear positive effect of the higher molecular weight (4 million relative to 300.000) of MMW CPAAM. However the samples taken after sedimentation, figure 6.9 (lower parts) and 6.10, indicate a positive effect of molecular weight on the CPAAMs ability to produce settleable flocs.

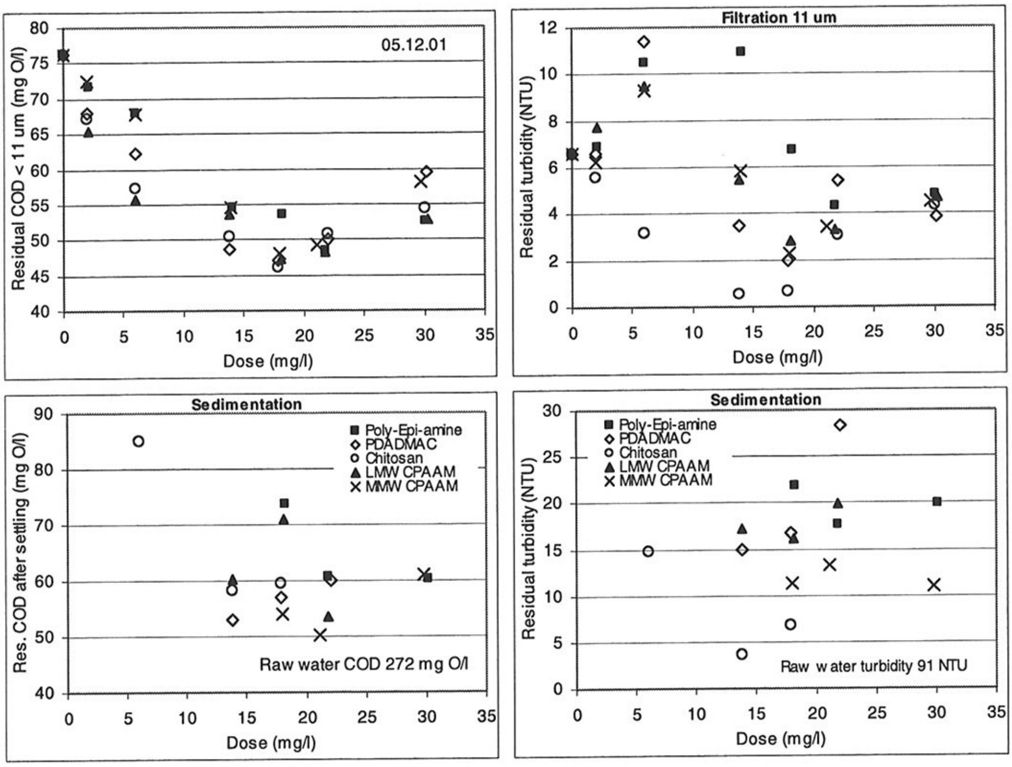


Figure 6.9. Comparison of residual COD and turbidity in supernatant after settling and in filtrate after filtration through11 μm paper filter.

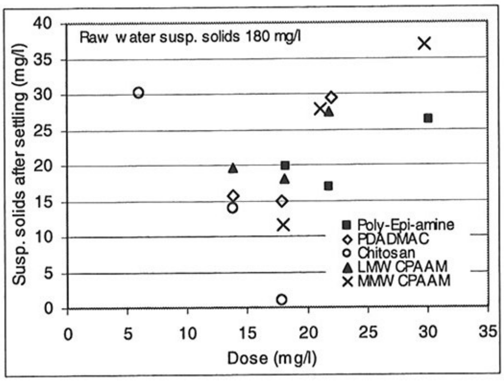


Figure 6.10. Suspended solids after settling as function of polymer dose for the three best results (based on visual observations) for each polyelectrolyte.

It is remarkable that chitosan, with a molecular weight of 80.000, again appears to stand out as the superior flocculant. Having a charge density comparable to that of the CPAAMs, and a substantially lower molecular weight than all the other polyelectrolytes tested, the results seem to indicate that some feature of the chemical composition of chitosan relative to that of CPAAM has a strong effect on its efficiency as a flocculant.

6.3.3 Main findings on flocculation and interaction of polyelectrolyte with different size fractions of organic material

- Comparison of results with low (300 000) MW and medium (4 000 000) MW CPAAM indicated no effect of MW on the ability to form flocs separable by filtration through 11, but a positive effect on the ability to produce settleable flocs.

- Results on coagulation of dissolved COD, residual COD and turbidity after filtration through 11 μm and settling, as well as suspended solids after settling, indicated that chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate matter, to flocs separable by filtration through 11 μm paper filter as well as by settling than the other polyelectrolytes tested.

6.4 Cationic polyelectrolyte coagulant combined with metal salt coagulant

A set of experiments was performed in order to demonstrate the effect of combining a cationic polyelectrolyte coagulant and a metal salt coagulant. The experiments were performed in parallel with lab scale batch flotation experiments to allow for a comparison between results obtained with the jar test-sequential filtration protocol and an experimental methodology utilizing a more realistic particle separation technique. The lab -scale batch flotation experiments were part of a contract project at SINTEF (Melin *et al*, 2002) investigating a treatment process for wastewater combining a biofilm process with coagulation and dissolved air flotation using combinations of metal salt and polyelectrolyte coagulants (presented schematically in figure 4.2, sub chapter 4.4.2).

Four different dosages (including zero) of iron chloride sulphate were tested in combination with a 2 mg/l dosage of PDADMAC at ambient raw water pH. The reason for performing the experiments at ambient raw water pH, and not at pH 6 as the main experiments on wastewater, were to allow for direct comparisons with the flotation experiments. However, two experiments were performed using 2 mg/l PDADMAC + 0,1 mmol/l Fe (5,6 mg Fe/l) with adjustment of raw water pH prior to coagulation in order to investigate the effect of pH. Raw water for the experiments were as usual collected from the outlet of the MBBR, as described in sub chapter 4.4.2. The composition of the raw water batch used in the experiments reported in this sub chapter is given in tables 4-7 and 4-8, sub chapter 4.4.2.2.

6.4.1 Combined use of PDADMAC and iron chloride sulphate

The effect of combining a low dose (2 mg/l) of PDADMAC with incremental dosages of iron chloride sulphate on coagulation is presented in figure 6.11. It should be noticed that the zero-value on the abscissa represents dosage of 2 mg/l PDADMAC alone (not zero dosage). Experiments were performed at ambient raw water pH, which means a pH range declining from 8,2 (only PDADMAC) to 7,7 (PDADMAC + 0,3 mmol Fe/l) with increasing iron chloride sulphate dosage.

Figure 6.11 (below) shows that supplementing a low dose (2 mg/l) of PDADMAC with small dosage increments of iron chloride sulphate has a positive effect on coagulation of dissolved organic substances as well as formation of flocs larger than 11 µm, measured as removal of COD after filtration through 0,1 µm and 11 µm respectively. Substantial increases relative to the sole use of PDADMAC in removals of COD and turbidity after filtration through 11 µm are seen at supplementary iron chloride sulphate dosages of about 5,6 mg Fe/l. Removal of UV-absorbing substances after filtration through 0,1 µm membrane filter shows a clear response to supplementary additions of iron chloride sulphate with substantial increase in removal already at the lowest iron chloride dosage.

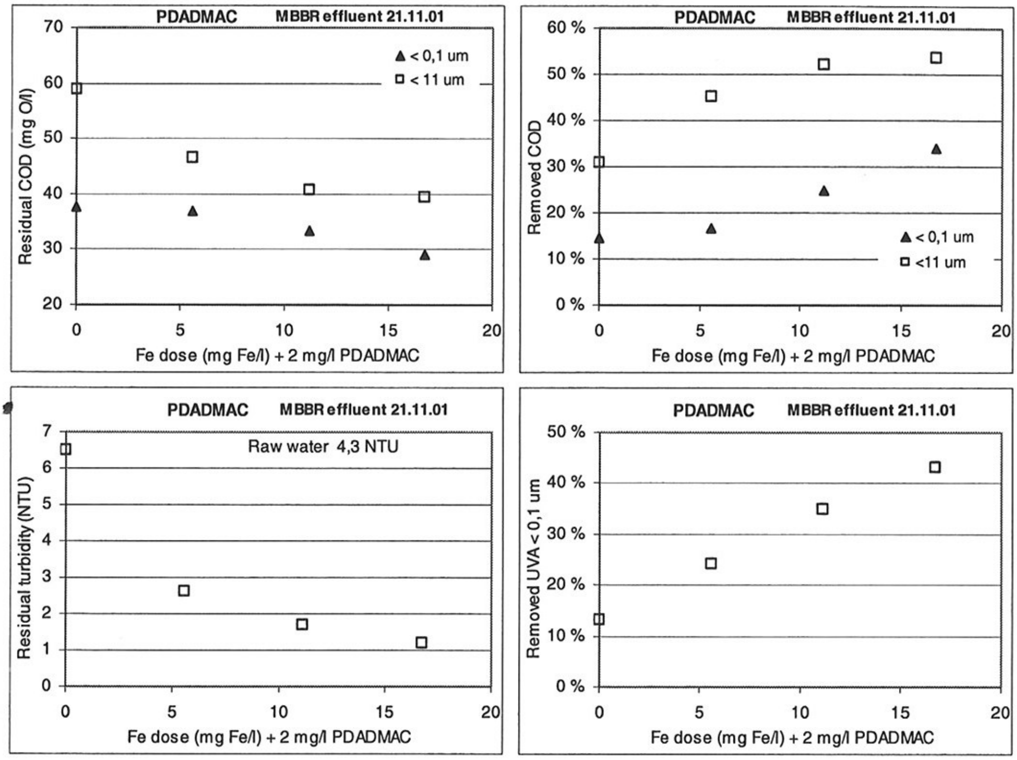


Figure 6.11. Removal of COD, turbidity and UV-absorbing substances from wastewater by combined use of inorganic (iron chloride sulphate) and organic polycationic coagulant PDADMAC. Top: Residual and relative removal of COD after filtration through 11 µm and 0,1 µm respectively. Bottom: Residual turbidity after filtration through 11 µm paper filter (left) and relative removal of UV-absorbing substances after filtration through 0,1 µm membrane filter.

6.4.2 Effect of coagulation pH

In the same set of experiments as reported above, the effect of lowering coagulation pH was tested by repeating the dosage point 2 mg/l PDADMAC + 0,1 mmol/l Fe (5,59 mg Fe/l) on raw waters with pH's adjusted to 7,2 and 5,5 (resulting coagulation pH) by addition of conc. hydrochloric acid. The results with respect to residual COD and relative removal of COD after filtration through 11 µm paper filter and 0,1 µm membrane filter as well as residual turbidity after filtration through 11 µm and relative removal of dissolved (< 0,1 µm) UV-absorbing substances are presented in figure 6.12 below.

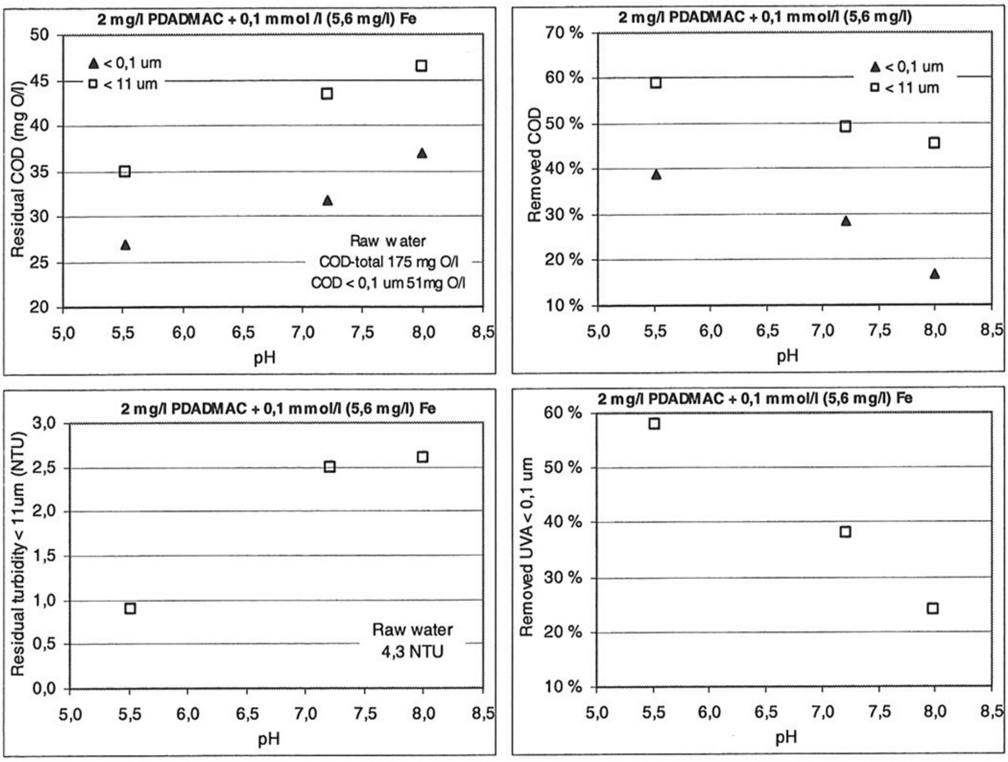


Figure 6.12. Effect of coagulation pH on the removal of COD, turbidity and UV-absorbing substances from wastewater by combined use of inorganic (iron chloride sulphate) and organic polycationic coagulant PDADMAC. Top: Residual and relative removal of COD after filtration through 11 µm and 0,1 µm respectively. Bottom: Residual turbidity after filtration through 11 µm paper filter (left) and relative removal of UV-absorbing substances after filtration through 0,1 µm membrane filter.

Figure 6.12 shows a strong influence of pH on coagulation of dissolved organic matter as well as on flocculation of particulate matter and new-formed aggregates. Both the moderate reduction of pH from 8,0 to 7,2 as well as the reduction further down to pH 5,5, which is in the optimal region with respect to the efficiency of iron chloride sulphate, give rise to substantial increases in the coagulation of dissolved organic matter (measured as removal of COD and UVA after filtration through 0,1 µm membrane filter) as well as flocculation to particle sizes larger than 11 µm (measured as removal of COD and turbidity after filtration through 11 µm paper filter).

Comparing with the results reported in the previous sub chapter, it is of interest to observe that just the moderate reduction of pH to 7,2 had a greater positive effect on coagulation of dissolved organic matter than the doubling of iron chloride sulphate dose from 5,59 (0,1 mmol/l) to 11,17 mg Fe/l (0,2 mmol/l). With respect to removal of COD after filtration through 11 μm the effects were of approximately the same magnitude, whereas with respect to the corresponding removal of turbidity increasing iron chloride sulphate dosage had a larger positive effect than the pH reduction.

Results obtained with combined use of PDADMAC and iron chloride sulphate are not directly comparable to the results obtained with PDADMAC as sole coagulant in the main experiments (sub chapter 6.1). The experiments were performed on different batches of MBBR effluent, differing in concentrations of dissolved and particulate organic matter as well as pH. However, for the sake of a rough comparison it could be noted that in the main experiments at pH 6, between 25 and 30% removal of COD after filtration through 0,1 μm membrane filter were obtained with a dosage of 15 mg/l PDADMAC. At pH 5,5, with a raw water composition between those of the two main experiments, 2 mg/l PDADMAC combined with 11,2 mg Fe/l (0,2 mmol Fe/l) as iron chloride sulphate, gave a corresponding removal of dissolved COD of close to 40%. This appears partially to support hypothesis F, stated in sub chapter 3.1 and in the introduction to chapter 6, also with respect to dissolved organic substances in wastewater (biofilm reactor effluent): *The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.*

6.4.3 Comparison with batch flotation experiments

The experiments described above were performed in parallel with lab scale batch flotation experiments to allow for a comparison between results obtained with the jar test-sequential filtration protocol and an experimental methodology utilizing a more realistic particle separation technique. The lab -scale batch flotation experiments were part of a contract project at SINTEF (Melin *et al*, 2002) according to a protocol described in chapter 4.4.4 and with the same raw water (split collection of MBBR effluent) and coagulants as in the filtration experiments.

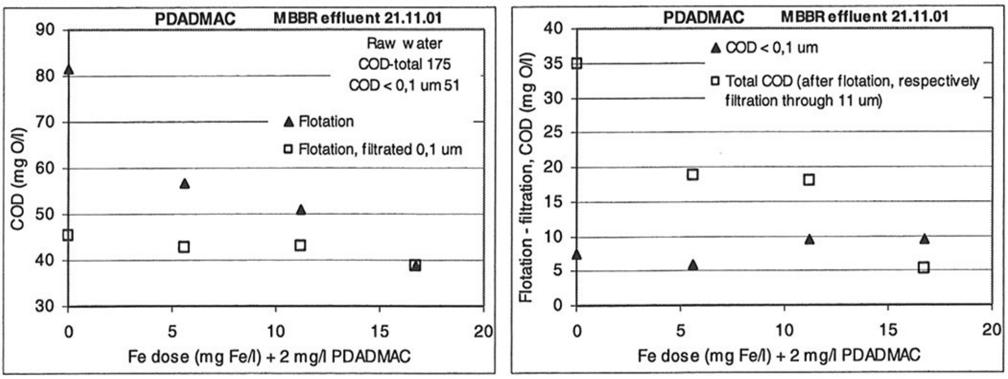


Figure 6.13. Results from flotation experiments with respect to dissolved and total organic matter measured as COD (left), compared to results obtained by the standard experimental protocol used in this study as the difference of flotation results – filtration results (right). Experiments were performed in parallell on the same raw water and with the same coagulants (iron chloride sulphate and PDADMAC).

The graphs indicate that a higher removal of COD is obtained with paper filtration (11 μm) than flotation as particle separation method. The difference between removals of COD obtained by filtration relative to filtration (11 μm) appear to depend on iron chloride sulphate dosage, approaching the results obtained with paper filtration as the supplemental iron dosage is increased from 5,59 mg Fe/l (0,1 mmol Fe/l) to 16,18 mg Fe/l (0,3 mmol Fe/l). With respect to removal of dissolved COD (< 0,1 μm) the difference between results obtained by flotation and filtration is more or less constant over the entire iron dosage range (0 – 0,3 mmol/l). This appears to imply a systematic difference in coagulation efficiency obtained with the two different experimental protocols. It seems probable that this could be related to differences in the method of adding, and thereby mixing of, the coagulants. In the filtration experiments coagulants were added with automatic pipette in the most turbulent region of the jars, whereas in the flotation experiments the coagulants were added with syringes, tippets not submerged, to the top of the jars (where turbulence is substantially lower). It is also probable that the difference in addition/mixing of coagulants has had an effect on the difference in results obtained with filtration vs. flotation with respect to removal of total COD.

6.5 Batch flotation experiments with MMW CPAAM, chitosan and iron chloride sulphate

The experiments reported in this chapter were originally intended and designed to investigate the effect of molecular weight and charge density of polyacrylamides as coagulants and flocculants, alone and in combination with a metal salt coagulant (iron chloride sulphate) for wastewater treatment. The polyacrylamide polymer test set was especially designed by Kemira for the contract project at SINTEF (Melin *et al*, 2002) investigating the combination of a high rate moving bed biofilm process with a coagulation-flotation process for removal of organic and suspended matter from wastewater (as described in sub chapter 4.4.2). In short the test set consisted of three series of polyacrylamides with MWs of 4, 5 and 6 million Dalton and with charge densities of 3,0 , 3,5 and 4,0 meq/g within each series. The experiments were designed according to a Box Benkhen design as described in chapter 4 in order to facilitate analysis of independent effects of charge density and molecular weight with ANOVA. Unfortunately the experimental uncertainty of the experiments, as found by repetitions of the centre point in the design, was to high (ranging from 5% to 16% depending on analysis parameter) relative to the individual effects of charge density and MW for these to be significant at the 95% probability level.

However two chitosan coagulants (F_A 0,37 and 0,95) were included in the experiments (although not in the Box Benkhen design) in order to investigate how these performed relative to cationic polyacrylamides in flotation experiments. This provided some interesting and rather surprising results with respect to the performance of chitosan as a flocculant, alone and in combination with iron chloride sulphate. The experiments were performed at ambient raw water pH (ranging from 7,9 to 7,7 with an average of 7,8, depending on iron chloride sulphate dosage). Chitosan, being a weak polycation with a pK_a of the charged amino group of 6,6, has a substantially reduced solubility and a theoretical cation charge density of merely 0,2 meq/g (chitosan F_A 0,05) at this pH. In figure 6.14 the results from batch flotation experiments with chitosan FA 0,05, alone and in combination with 0,2 mmol Fe/l (11,17 mg Fe/l) iron chloride sulphate, are compared with corresponding averaged results obtained with the cationic PAAM test set. The averaged results reported for CPAAM represent the average of all results obtained with the different polyelectrolytes in the test set for each individual dosage.

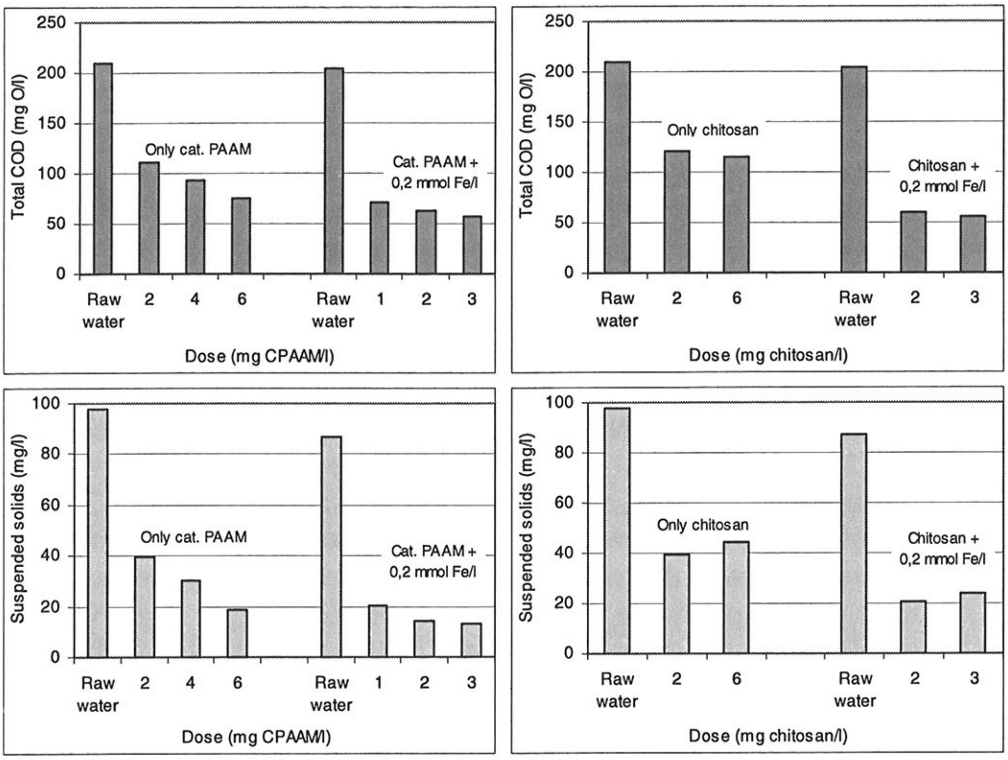


Figure 6.14. Removal of COD and suspended solids from wastewater by flotation after coagulation with cationic polyelectrolytes (chitosan and MMW CPAAM) alone and in combination with iron chloride sulphate respectively. Experiments with polyelectrolytes alone and in combination with iron chloride sulphate were performed on different dates and with different raw waters. Results reported for cationic CPAAM represent the average of all results obtained with the different polyelectrolytes in the Kemira CPAAM testset for each individual dosage

Figure 6.14 shows that chitosan alone removes substantially less COD and suspended solids than the cationic PAAM. However, in combination with iron chloride sulphate removals with chitosan and MMW CPAAM are comparable. Results (Melin *et al*, 2002) from the contract project referred to above clearly indicated positive effects of cationic charge density as well as of molecular weight on the efficiency of cationic polyelectrolytes as coagulants and flocculants in combination with iron chloride sulphate for the flotation of wastewater. Taking into account that chitosan would be expected to be more or less insoluble at this pH, and at best having more than a ten-fold lower charge density as well as molecular weight than the CPAAMs, the good flocculation exhibited by chitosan in combination with a relatively low dosage of iron chloride sulphate is quite remarkable.

With reservations on the low number of experiments performed, the results appear to indicate that some feature of the chemical structure of chitosan exhibits an unusual efficiency with respect to flocculation of biofilmreactor effluent when used in combination with iron chloride sulphate. Similar results, with respect to the efficiency of chitosan as a flocculant, were also observed in the jar test/filtration experiments on biofilm reactor effluent (sub chapter 6.3) as well as on humic water (sub chapters 5.1.3 and 5.1.4). It would be of great interest to follow up on these findings with further experiments.

7 COMPARISON OF COAGULATION OF DISSOLVED ORGANIC SUBSTANCES IN HUMIC WATER AND BIOFILMREACTOR EFFLUENT

One of the ambitions of this work was to determine the performances of the different polyelectrolytes in two substantially different types of waters. In sub chapter 3.1 the following hypothesis (G) was stated in order to specify the approach the problem.

- *A significant portion of the dissolved organic substances in wastewater is made up of humic-like substances and the coagulation of these by polyelectrolytes can be explained accordingly to that of humic substances in surface water*

The intention of this chapter has been to attempt to draw some lines between findings from the experiments on coagulation and flocculation of the particle free, relatively homogeneous humic water and particle rich, more heterogenic wastewater (biofilm reactor effluent). The inclusion of UVA and TOC as routine analytical parameters in the experiments on wastewater was carried out partly in order to make this possible.

In the experiments on humic water at pH 6 all the polyelectrolytes tested appeared to reach approximately the same maximum colour and UVA removal level, but different dosages were required to reach the same levels of removal. This was shown to be an effect of polyelectrolyte charge density on coagulation of dissolved humic substances, and furthermore shown to be predominantly a result of mere differences in amounts of cationic charge equivalents added. The results with respect to the effect of polyelectrolyte charge density on efficiency of polyelectrolytes as coagulants for dissolved organic matter in biofilm reactor effluent were unclear. Results obtained with the raw water batch with the highest content of UV-absorbing substances relative to dissolved and total organic material measured as COD (08.11.01) showed differences in polymer dose efficiency with respect to coagulation of UV-absorbing substances, and a tendency similar to that observed in humic water. This could be interpreted to partly be in support of hypothesis H above. However, with the other wastewater batch, exhibiting substantially higher particle contents and lower relative contents of dissolved organic matter, this effect could not be reproduced. Thus no strong conclusions can be dawn.

With respect to flocculation the most interesting finding was how the performance of chitosan deviated from the other polyelectrolytes tested. This was evident both in the experiments on humic water and on wastewater. In the experiments on humic water all polyelectrolytes tested showed comparable removals of colour, UVA and TOC as well as residual turbidity after filtration through 11 μm paper filter at low dosages (sub optimal with respect to aggregate formation). At higher dosages (needed to obtain maximum aggregate formation) however, significant differences were observed indicating that aggregates produced with chitosan exhibited far better flocculation properties. Also, chitosan exhibited a high level of removals after filtration through 11 μm paper filter over a substantially wider dosage range than the other polymers tested. In the experiments on wastewater, chitosan showed net removal of turbidity even at low doses, whereas coagulation of dissolved organic substances with the synthetic polycations was accompanied by an immediate and substantial increase in residual turbidity. Furthermore, the results indicated that chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate matter, to flocs separable by filtration through 11 μm paper filter as well as by settling, than the other polyelectrolytes tested.

As mentioned in the introduction to this chapter the inclusion of dissolved UVA and TOC as analytical parameters in the experiments on wastewater opens for a more direct and quantitative comparison of polyelectrolyte performances as coagulants in humic water and wastewater. Attempts on this are presented graphically in figures 7.1 and 7.2 below. The humic raw water and wastewater represent very different systems with respect to heterogeneity in composition of dissolved organic matter as well as particle concentrations and size distributions. In the humic water system the polyelectrolytes can initially only interact with dissolved organic substances, and these constitute a substantially lower mass than the total mass of dissolved organic substances in the wastewater systems. In the wastewater the polyelectrolytes can also interact with a large number of different sized particles. Intuitively one would therefore expect these systems to exhibit very different polymer dosage responses with respect to coagulation of dissolved organic substances.

In figure 7.1 absolute removals of dissolved UV-absorbing substances after coagulation with PDADMAC and chitosan in humic water and wastewater are presented both as functions of absolute polymer dose (left) and dissolved TOC specific polymer dose (right).

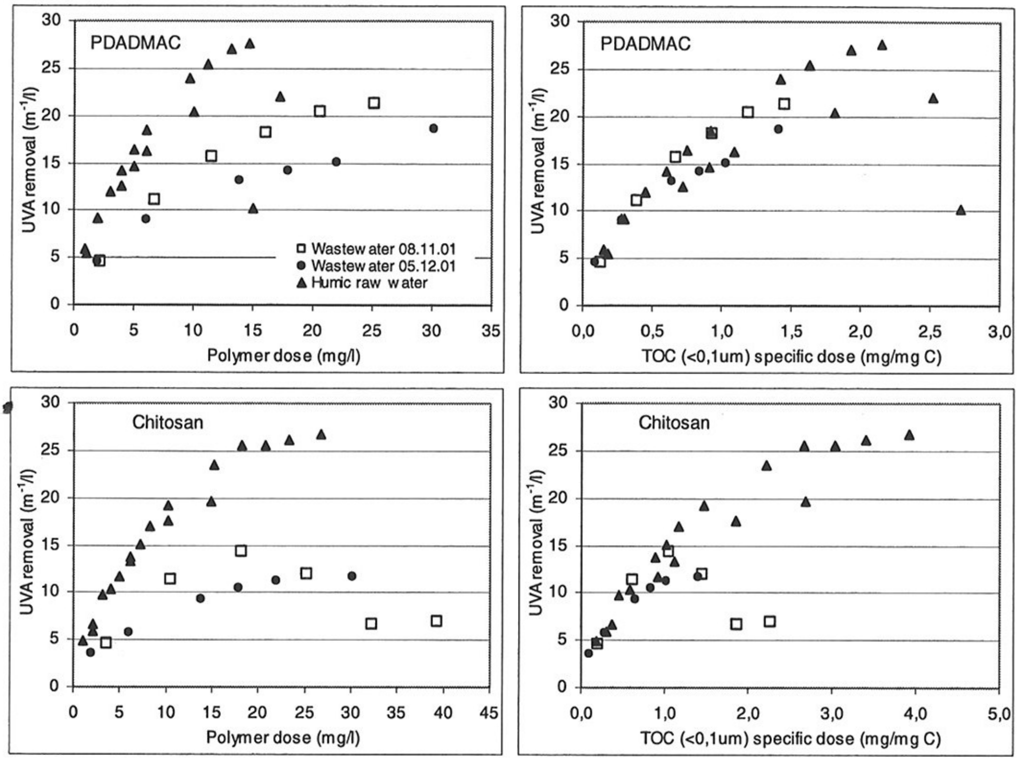


Figure 7.1. Coagulation of UV-absorbing dissolved susbtances in humic water and wastewater with PDADMAC (top) and chitosan F_A 0,05 (bottom) presented as absolute removals after filtration through 0,1 μm as functions of absolute polymer dose (left) and dissolved TOC specific polymer dose (right).

Focusing first on the left part of figure 7.1, the dosage responses of PDADMAC as well as chitosan in humic water versus in wastewater (biofilm reactor effluent) are quite as expected. Being more concentrated systems with respect to dissolved organic matter as well as particles; the wastewaters appear to "consume" more of the polyelectrolytes leaving less to interact with UV-absorbing substances.

The same tendency can be observed when comparing results with wastewater batch 08.11.01 with the results of the more concentrated batch 05.12.01. However, when plotting the dosage responses as functions of dissolved TOC specific dosages (right part of figure 7.1) it is interesting to observe the degree of similarity exhibited in these very different systems. Interesting because in the wastewaters the dissolved portions of organic matter represent only a relatively small fraction of the total matter the polyelectrolytes can be assumed to interact with.

Another feature that warrants attention is the dosage response exhibited within different batches of humic water, observable as the group of points displaced downwards with respect to UVA-removal as functions of absolute polymer dose as well as TOC specific polymer dose. These points all belong to a set of experiments performed on a humic raw water batch with significantly lower concentration of dissolved organic substances than the other raw water batches (80 and 87 % of standard concentrations with respect to coloured and UV-absorbing substances and TOC respectively) and indicate that absolute as well as TOC specific dose efficiency improves with concentrations of dissolved organic substances. However this raw water batch exhibits far less deviation from the other batches of humic raw water with respect to total concentration of dissolved organic substances than the wastewater batches.

This appears to imply that the coagulation of UV-absorbing substances with cationic polyelectrolytes at pH 6 is equally well explained in terms of a dosage stoichiometry with respect to dissolved TOC in wastewater (biofilm reactor effluent) as in humic water; thus offering partial support for hypothesis G.

In order to investigate more specifically whether the dosage response with respect to coagulation of dissolved UV-absorbing substances could be explained even better by the concentration of UV-absorbing substances rather than TOC in the raw waters, absolute removal of dissolved UV-absorbing substances have been plotted as function of UVA specific dose in figure 7.2.

If the dose efficiency with respect to coagulation of UV-absorbing substances were to be controlled only by the concentration of UV-absorbing substances in the raw waters this should either cause all the data points in figure 7.2 (below) to be concentrated along one line or show increasing UVA-specific dose efficiency as function if increasing UVA in the raw waters (wastewater 05.12.01 > wastewater 08.11.01 > "normal" humic water > less concentrated humic water). This is not observed in figure 7.2. A higher UVA-specific dose efficiency is observed for "normal" humic water than for humic water with lower concentration of UV-absorbing substances, but the wastewaters show a lower UVA-specific dose efficiency than the humic waters although having higher concentrations of UVA-absorbing substances.

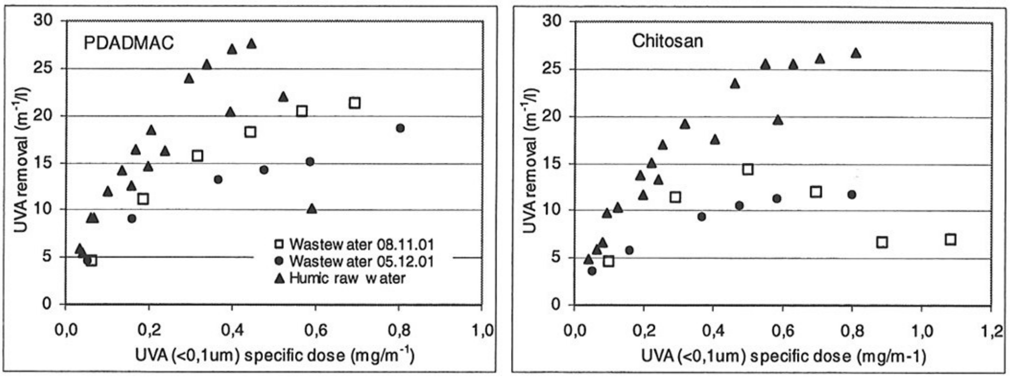


Figure 7.2. Coagulation of UV-absorbing dissolved susbtances in humic water and wastewater with PDADMAC (left) and chitosan F_A 0,05 (right) presented as absolute removals after filtration through 0,1 µm as functions of UVA specific polymer dose (right).

Comparing again with figure 7.1, the coagulation of UV-absorbing or humic substances in these very different raw water systems appears to be better explained by the a dosage stoichiometry with respect to total concentration of dissolved organic substances in the raw water (measured as dissolved TOC) than with respect to the concentrations of humic substances (measured as UVA) specifically.

Finally it is interesting to compare polymer dose efficiency with respect to coagulation of the bulk of dissolved organic substances (measured as TOC < 0,1 µm) in humic water and wastewater. In figure 7.3 (below) absolute removals of dissolved TOC after coagulation with PDADMAC and chitosan in humic water and wastewater are presented both as functions of absolute polymer dose (left) and dissolved TOC specific polymer dose (right).

Again the results are somewhat surprising. Intuitively one could expect the amount of particles in wastewater relative to humic water to have a strong influence on the interactions of polymers with the dissolved organic substances. The substantial additional surface area to which the polymers can adsorb could well be expected to cause the polyelectrolytes to exhibit lower dose efficiencies (absolute as well as TOC-specific) with respect to coagulation of dissolved organic substances in the wastewaters than in the humic water.

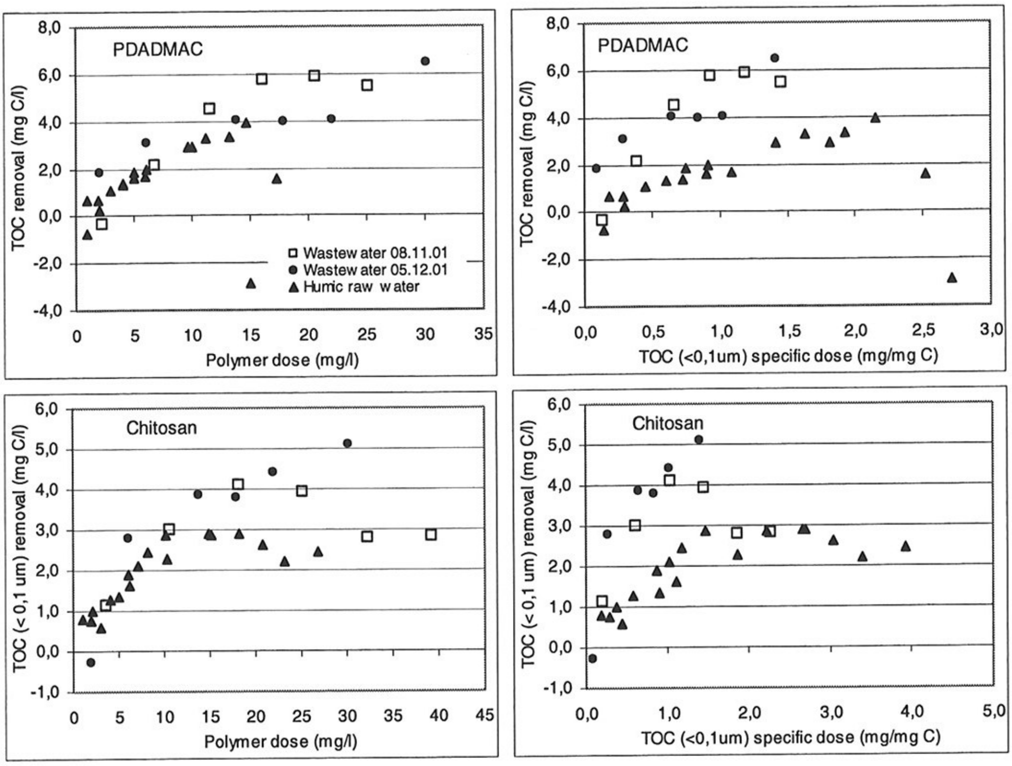


Figure 7.3. Coagulation of dissolved (< 0,1 µm) TOC in humic water and wastewater with PDADMAC (top) and chitosan F_A 0,05 (bottom) presented as absolute removals after filtration through 0,1 µm as functions of absolute polymer dose (left) and dissolved TOC specific polymer dose (right).

This appears not to be the case for the results presented in figure 7.3. Dose efficiency with respect to removal of dissolved organic substances does not appear to be negatively influenced by the large amounts of particles present in the wastewaters. On the contrary, the TOC-specific dose efficiency is seen to be higher in the particle rich wastewaters than in the humic water.

A straightforward explanation to this finding is hard to identify. The results from the experiments on humic water seemed to indicate that higher concentrations of dissolved organic substances in the raw water increases the TOC specific dosage efficiency. The results from the experiments on biofilm reactor effluent seemed to indicate that the coagulation of dissolved organic substances is positively influenced by the presence of particulate matter. Furthermore, it has been shown (sub chapter 5.4) that the character of the dissolved organic matter itself probably plays an important role in how it interacts with cationic polyelectrolytes. At present it is not possible to determine the relative importance of these different factors.

The conclusion appears to be that the results point to some interesting similarities, as well as differences, in the way cationic polyelectrolytes interact with dissolved organic substances in widely different waters, and that further experiments are necessary to fully understand the mechanisms involved.

8 SUMMARY AND CONCLUSIONS

Cationic polyelectrolytes of the following types were selected for testing as coagulants in jar test experiments using sequential filtration through 11 μm, 1,2 μm, 0,45 μm and 0,1 μm as the particle separation methode: poly-Epi-amine, PDADMAC, cationic polyacrylamide (low and medium molecular weight) and chitosan (F_A=0,05 and F_A=0,37).

A summary of the most important findings from the experiments on humic water and biofilm reactor effluent as raw waters is presented in sub chapters 8.1 through 8.9. Final conclusions are drawn in sub chapter 8.10.

8.1 General performance observations – coagulation

General performance of the tested polyelectrolytes as coagulants for NOM in humic water

- All polyelectrolytes tested were efficient in coagulating NOM (measured as removal of dissolved NOM after filtration through 0,1 μm membrane filter) and reached approximately the same maximum levels of coagulation.

- Colour removals after filtration through 0,1 μm up to 95% were observed for all polyelectrolytes. TOC removals were lower reaching a maximum of 45-50%.

- High dosages (10 to 20 mg/l) were required to achieve maximum coagulation of NOM, but coagulation levels adequate for most practical purposes (65 to 85%) could be achieved with substantially lower dosages (approximately 3 to 7 mg/l).

- For all polyelectrolytes, the dosage responses with respect to coagulation of coloured, UV-absorbing and bulk NOM (measured as TOC) were very similar

General performance of the tested polyelectrolytes as coagulants for dissolved organic substances in biofilm reactor effluent

- 30-35% and 20-25% removal respectively (for experiments performed on 08.11.01 and 05.12.01) of dissolved organic matter measured as COD < 0,1 µm was achieved with all the cationic polyelectrolytes tested.

- The results with respect to dissolved COD or TOC gave no sound basis for distinguishing between the relative coagulation efficiencies of the different polyelectrolytes.

- As was observed in coagulation of humic water, relative removals of UV-absorbing dissolved organic substances were in general substantially higher than removals of the bulk of dissolved organic substances, measured as COD or TOC. Removals with respect to TOC after filtration through 0,1 µm were comparable to those obtained for COD.

8.2 The relationship between coagulation of dissolved organic substances and flocculation of aggregates in humic water

Chapter 3.1 stated the following hypothesis (A) concerning the relationship between coagulation of dissolved organic substances and flocculation of aggregates:

> *Hypothesis A*
> *Coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima. That is, the polyelectrolyte dosage providing maximal coagulation of dissolved organic substances is not identical to the dosage providing aggregates with the best flocculation properties.*

- The results supported this hypothesis. The polyelectrolyte dosage providing maximal coagulation of dissolved organic substances lies substantially higher than the dosage providing aggregates with the best flocculation properties.

8.3 General performance observations - flocculation

Flocculation properties of aggregates formed by coagulation of NOM with different polyelectrolytes in humic water

- Optimal dose for floc growth of NOM-polymer aggregates appeared not to be governed by cationic charge dose, but rather by the chemical composition of the polyelectrolytes.
- The results showed substantial differences between the polyelectrolytes with respect to the ability to create flocs larger than 11 μm. With the exception of chitosan, the highest observed removal after filtration through 11 μm for each polyelectrolyte appeared to follow the same internal ranking as the polyelectrolyte charge densities (poly-Epi-amine > PDADMAC > CPAAM).
- Chitosan appeared to produce aggregates with NOM with better flocculation properties than the other polyelectrolytes tested.

Interaction of polyelectrolyte with different size fractions of COD in biofilm reactor effluent

- With the synthetic polyelectrolytes the results indicated that acceptable flocculation of particles and new-formed aggregates first takes place after all coagulable dissolved organic matter has been coagulated.
- Chitosan appeared to be more capable of acting both as coagulant and flocculant than the synthetic polyelectrolytes at low dosages.
- Comparison of results with low (300 000) MW and medium (4 000 000) MW CPAAM indicated no effect of MW on the ability to form flocs separable by filtration through 11, but a positive effect on the ability to produce settleable flocs.
- The results indicated that chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate

matter, to flocs separable by filtration through 11 μm paper filter as well as by settling, than the other polyelectrolytes tested.

- Results from dissolved air flotation experiments showed that chitosan, when used in combination with iron chloride sulphate, is an efficient flocculant also at a pH (8,0) at which it has practically no charge and a severely reduced solubility.

8.4 The effect of polyelectrolyte charge density

Differences in the polyelectrolytes efficiencies as coagulants and the nature of the effect of polyelectrolyte charge density on coagulation of NOM in humic water

Chapter 3.1 stated the following hypotheses (B and C) concerning differences in the polyelectrolytes efficiencies as coagulants and the nature of the effect of polyelectrolyte charge density on coagulation of dissolved organic substances:

> *Hypothesis B*
> *Differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain*

- The results from the main experiments on humic water at pH 6 supported this hypothesis:

- Differences in coagulation dose efficiency (% NOM coagulated per mg polymer) between the different polyelectrolytes were primarily an effect of differences in polyelectrolyte charge density.

> *Hypothesis C*
> *With respect to coagulation of dissolved humic substances the effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such.*

- The results from the main experiments on humic water at pH 6 supported this hypothesis:

- The effect of polyelectrolyte charge density on coagulation of coloured and UV-absorbing NOM were predominantly explained by the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not by the differences in the spatial distribution of charge as such.

However, experiments performed with PDADMAC and two different chitosans ($F_A = 0{,}05$ and $F_A = 0{,}37$) at pH 4 showed a more complex picture.

- Comparison of the results for the two different chitosans appeared to be in support of hypotheses B and C both at pH 6 and pH 4.

- Comparison of results for chitosan and PDADMAC at pH 4 indicated that the effect of charge addition that was dominating at pH 6 was less pronounced at pH 4.

- It was suggested that that there may exist alternative mechanisms for the interaction between NOM and cationic polyelectrolytes, and that the relative importance of these depend on pH and the charge density of the NOM.

The effect of polyelectrolyte charge density on coagulation of dissolved organic substances in biofilm reactor effluent

The results with respect to the effect of polyelectrolyte charge density on their efficiencies as coagulants for dissolved organic matter were unclear.

Results obtained with the raw water batch with the highest content of UV-absorbing substances relative to dissolved and total organic material measured as COD (08.11.01) showed differences in polymer dose efficiency with respect to coagulation of UV-absorbing substances, and a tendency similar to that observed in humic water. This tendency with respect to the effect of polymer charge density appeared, however, not to be reproduced in results obtained 05.12.01.

8.5 The effect of polyelectrolyte molecular weight

The effect of polyelectrolyte molecular weight on coagulation of NOM in humic water

Chapter 3.1 stated the following hypothesis (D) concerning the effect of polyelectrolyte molecular weight on coagulation of dissolved organic substances:

> *Hypothesis D*
> *Differences in molecular weight have a subordinate, if any, effect on the coagulation of dissolved organic substances*

The results on low molecular weight CPAAM compared to those of medium molecular weight CPAAM supported this hypothesis, showing no indications of a positive effect of increased molecular weight on coagulation efficiencies.

8.6 Effect of pH

The effect of pH on coagulation of NOM with cationic polyelectrolytes in humic water

Chapter 3.1 stated the following hypotheses (E-1 and -2) concerning the effect of pH on coagulation of dissolved humic substances with cationic polyelectrolytes:

> *Hypothesis E-1*
> *Due to increased protonation of the carboxyl groups, and thus reduced anionic charge density, of the humic substances, lowering of pH from 6 to 4 results in improved dose efficiencies with respect to coagulation of NOM with cationic polyelectrolytes.*

The results obtained with PDADMAC and the more highly acetylated chitosan (F_A=0,37) supported hypothesis E-1. The effect of pH was less significant with the “standard” chitosan (F_A=0,05).

Hypothesis E-2

With chitosan a reduction of pH will also result in a gain in cationic charge density due to protonation of the amine groups. Therefore the effect of reducing pH on polymer dose efficiency will be more pronounced for a weak polycation such as chitosan than for a strong polycation such as PDADMAC.

No evidence was found to support hypothesis E-2. The effect of pH on coagulation dose efficiency was far less pronounced with chitosan than with PDADMAC.

With PDADMAC the highest observed removal after filtration through 0,1 μm decreased slightly (from about 95% to about 90%) with respect to colour, and more substantially (from about58% to about 39%) with respect to dissolved TOC. The point of optimal dosage (with respect to maximum colour removal) shifts substantially downwards, from approximately 2,2 to 0,9 mg/mg TOC. It was suggested that a fraction of the NOM is rendered more or less deionised (due to protonation of carboxylic groups) as pH is reduced and that the neutralised fraction of NOM is incapable to interact electrostatically with the cationically charged polyelectrolyte.

8.7 The effect of degree of acetylation (F_A) of chitosans on coagulation of NOM in humic water

The effect of the degree of acetylation of chitosans was, as expected, in accordance with hypotheses B and C, stated in sub chapter 3.1 (and 8.2 above), regarding the effect of polyelectrolyte charge denity on coagulation of dissolved organic substances:

- The chitosan with the lowest degree of acetylation (F_A 0,05), and therefore the highest cationic charge density, exhibited higher polymer dose efficiency with respect to coagulation of humic substances than the more highly acetylated chitosan ($F_A = 0,37$).

- When the results on coagulation were plotted as function of cationic charge dose the differences in dose efficiency between the chitosans were more or less eliminated.

8.8 Combination of metal salt and cationic polyelectrolytes as coagulants for dissolved organic substances

Combination of metal salt and cationic polyelectrolytes as coagulants for NOM in humic water

Chapter 3.1 stated the following hypotheses (F) concerning the effect of combining a metal salt and a cationic polyelectrolyte as coagulants for dissolved organic substances:

> *Hypothesis F*
> *The dosage of a cationic polyelectrolyte coagulant necessary to obtain a given degree of coagulation and flocculation of dissolved organic substances can be reduced significantly when combined with a low dosage of a metal salt coagulant.*

The results appeared to be in support of hypothesis F showing that a high degree of coagulation of coloured NOM (75 and 70% for PDADMAC and chitosan respectively) could be achieved by combining a low dosage (2 mg/l) of cationic polyelectrolyte with a low dosage (2 mg Fe/l) of iron chloride sulphate. However, good flocculation properties (measured as removal after filtration through 11 μm paper filter) were only observed with at pH 5, and not at pH 6, at these dosages. The results gave no indications that a strong polycation (PDADMAC) performs principally different from a weak polycation (chitosan) in a low dosage combined polyelectrolyte – metal salt coagulant system.

Combination of metal salt and cationic polyelectrolyte as coagulants for dissolved organic substances in biofilm reactor effluent

Although not directly comparable, due to differences in raw water composition and pH, a combination of 2 mg/l PDADMAC with 11,2 mg Fe/l as iron chloride sulphate gave a higher degree of coagulation (40%) of dissolved organic substances, measured as COD, than 15 mg/l PDADMAC did in the main experiments at pH 6 (25 to 30% coagulation). This appears partially to support hypothesis F, stated in sub chapter 3.1 and above.

Furthermore a strong dependency on pH was demonstrated:

- Results from experiments combining a low dosage (2 mg/l) of PDADMAC with low dosages (5,59 to 16,8 mg Fe/l) of iron chloride sulphate showed a strong influence of pH on coagulation of dissolved organic matter as well as on flocculation of particulate matter and new-formed aggregates.
- A moderate reduction of pH from 8,0 to 7,2 had a greater positive effect on coagulation of dissolved organic matter than the doubling of iron chloride sulphate dose from 5,59 (0,1 mmol/l) to 11,17 mg Fe/l (0,2 mmol/l).

8.9 Effect of raw water composition / concentration

Effect of differences in concentration of dissolved and particulate COD in biofilm reactor effluent

Plots of results from the experiments performed on two different batches of biofilm reactor effluent (08.11.01 and 05.12.01) in the same graph indicated that the presence of particle surfaces and adsorption of polyelectrolyte to these surfaces did not negatively affect, by competing for the polyelectrolyte molecules, the coagulation of dissolved organic matter with polyelectrolyte. Rather, there appeared to be a positive effect of the presence of particulate matter on the polymer dose efficiency in coagulation of dissolved organic matter.

Comparison of coagulation of dissolved organic substances in humic water and in biofilm reactor effluent

One of the ambitions of this work was to determine the performances of the different polyelectrolytes in two substantially different types of waters. In sub chapter 3.1 the following hypothesis (G) was stated in order to specify the approach the problem.

> *A significant portion of the dissolved organic substances in wastewater is made up of humic-like substances and the coagulation of these by polyelectrolytes can be explained accordingly to that of humic substances in surface water*

Plots of absolute removals of dissolved UV-absorbing substances from humic water and biofilm reactor effluent in the same graph as function of TOC specific polyelectrolyte dose indicated that the coagulation of UV-absorbing substances with cationic polyelectrolytes at pH 6 is equally well explained in terms of a dosage stoichiometry with respect to dissolved TOC in biofilm reactor effluent as in humic water; thus offering partial support for hypothesis G.

Plots of absolute removals of dissolved TOC from humic water and biofilm reactor effluent in the same graph showed that the TOC-specific dose efficiency was higher in the particle rich biofilm reactor effluent than in the particle free humic water. Different explanations to this finding are suggested, but in any case it showes that high concentrations of particulate matter does not appear to negatively influence the coagulation of dissolved organic substances.

8.10 Conclusions

Jar test experiments on humic water using sequential filtration as the particle separation methode showed that:

- Coagulation of dissolved organic substances by polyelectrolytes and the subsequent flocculation of aggregates are two distinguishable processes with distinguishable dosage optima.
- The polyelectrolyte dosage providing maximal coagulation of dissolved organic substances lies substantially higher than the dosage providing aggregates with the best flocculation properties.

Results from experiments on humic water at pH 6 indicated that:

- The differences in efficiencies of the different polyelectrolytes as coagulants for NOM are predominantly related to differences in charge density, not to differences in the chemical composition of the polymer chain.
- The effect of polyelectrolyte charge density is predominantly related to the additions of different amounts of charge equivalents when dosing equal amounts of polyelectrolytes with different charge densities, not to the spatial distribution of charge as such.

Experiments performed at pH 4 indicated that the effect of charge addition that was dominating at pH 6 is less pronounced at pH 4. It was suggested that that there may exist alternative mechanisms for the interactions between NOM and cationic polyelectrolytes (probably related to interaction between non-polar segments of NOM and polyelectrolyte), and that the relative importance of these depend on pH and the charge density of the NOM.

Results from experiments on biofilm reactor effluent indicated that:

- Chitosan forms aggregates with dissolved COD that more readily flocculate, internally or with other particulate matter, to flocs separable by filtration through 11 μm paper filter as well as by settling, than the synthetic polyelectrolytes tested.

Direct comparisons of results obtained on particle free humic water and two different bathces of particle rich biofilm reactor effluent indicated strong similarities in the dosage respons with respect to coagulation of dissolved humic-like (UV-absorbing) substances as well as dissolved TOC by cationic polyelectrolytes.

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APPENDIX - A

Calculation of theoretical stoichiometric charge density of chitosan as function of degree of acetylation (F_A) and pH

Chitosan is a heteropolymer consisting of uncharged N-acetylglucoseamine and weakly (pH-dependent) charged glucoseamine. It follows that the calculation of the stoichiometric charge density requires knowledge of the composition of the chitosan (fraction of acetylated units F_A), the pK_a value of the glucoseamine ammonium and the actual solution pH. The protonisation (and thereby the charge) of the glucoseamine ammonium is pH-dependent with pK_a between 6,2 and 7,0. The exact pKa-value of a weakly charged polymer depends on the ionic strength of the solution and, as the polymer itself may contribute significantly to this, also the actual polymer concentration (Smidsrød and Moe, 1995). For the polymer concentrations and ionic strength encountered in this work a pK_a value of 6,5 has been assumed to be appropriate.

It can be shown (Smidsrød and Moe, 1995) that the fraction α of charged (protonated) glucoseamine units takes the following function of pH:

$$\alpha = \frac{1}{\left(1 + \frac{K_a}{[H^+]}\right)}$$

and that the stoichiometric charge density per g chitosan takes the following function of α and F_A :

$$\text{Stoichiometric charge density, CD (C/g)} = \frac{e \cdot N \cdot \alpha \cdot (1 - F_A)}{F_A \cdot M_{\text{Acetylgluoseamine}} + (1 - F_A) \cdot M_{\text{Glucoseamine}}}$$

Where e = electron charge = $1{,}602 \times 10^{-19}$ C
N = Avogadros constant = $6{,}02 \times 10^{23}$
$M_{\text{Acetylglucoseamine}}$ = 203,2 g/mol
$M_{\text{Glucoseamine}}$ = 163,2 g/mol (for chitosan in the hydrogenated form)
$M_{\text{Glucoseamine}}$ = 197,6 g/mol (including Cl^- for chitosan in the chlorinated form)

It should be noted that the theoretical stoichiometric charge density obtained by these calculations, due to so called *counter ion condensation*, not necessarily reflects the *effective* charge density of the polyelectrolyte in solution (chapter 2.4.1.5).

APPENDIX - B

Uncertainty of measurements

The uncertainty of measurements most frequently used in this study was tested through repeated analysis on the same sample of humic water and wastewater. Uncertainty estimates are presented in tables A and B below.

Table A. Estimates of uncertainty for measurements on humic raw water. Uncertainties of TOC analysis have been estimated through repeated analysis of sample of treated water.

Parameter	Average	Standard deviation, s	Relative standard deviation, CV	95 % conf. interval for one replicate	Number of replicates, n
pH	6,83	0,05			5
Turbidity (<11 μm) (NTU)	0,53	0,03	6%	0,07	6
Colour (mg Pt/l) (<11 μm)	51,7	0,4	0,8%	0,8	6
Colour (mg Pt/l) (<1,2 μm)	51,6	0,5	0,9%	0,9	6
Colour (mg Pt/l) (<0,45 μm)	49,9	0,2	0,3%	0,3	6
Colour (mg Pt/l) (<0,1 μm)	48,9	0,3	0,6%	0,6	6
UVA (m^{-1}) (<11 μm)	25,2	0,2	0,8%	0,4	6
UVA (m^{-1}) (<1,2 μm)	25,7	0,02	0,1%	0,04	6
UVA (m^{-1}) (<0,45 μm)	25,4	0,02	0,1%	0,04	6
UVA (m^{-1}) (<0,1 μm)	25,2	0,02	0,1%	0,04	6
TOC (mg C/l) (<11 μm)	5,4	0,54	10 %	1,1	6
TOC (mg C/l) (<1,2 μm)	4,7	0,53	11 %	1,0	6
TOC (mg C/l) (<0,45 μm)	5,8	0,48	8 %	0,9	6
TOC (mg C/l) (<0,1 μm)	5,7	0,45	8 %	0,9	6

Table B. Estimates of uncertainty for measurements on bifilm reactor effluent.

Parameter	Average	Standard deviation, s	Relative standard deviation, CV	95 % conf. interval for one replicate	Number of replicates, n
Turbidity (<11 μm) (NTU)	4,1	0,09	2%	0,2	6
COD (mg O/l) (total)	101	2,9	3%	5,7	6
COD (mg O/l) (<11 μm)	44,6	3,3	7%	6,4	6
COD (mg O/l) (<1,2 μm)	45,1	3,9	9%	7,7	6
COD (mg O/l) (<0,1 μm)	33,3	1,6	5%	3,0	6
UVA (m^{-1}) (<0,1 μm)	47,2	0,3	1%	0,5	6
TOC (mg C/l) (<0,1 μm)	13,1	1,4	11 %	2,7	6

APPENDIX - C

Correction for pH in colour measurements

Measurements of colour and UV-absorbance show a dependency on pH that has to be corrected for when comparing measurements performed on solutions with differing pHs. For simplicity and as this work only includes comparisons of measurements performed on solutions with pH 6 and 4, corrections for ph has been achieved by first performing measurements at pH 4, adjusting pH to 6 by addition of a strong sodium hydroxide solution and then performing the same measurements at pH 6. The volumes added were very minute (2-3 drops at most) relative to the total volume (50 ml) so that dilution effects were considered to be negligible. This was carried out on samples of raw water and coagulated water with different degrees of removals as presented in figure A-1 below.

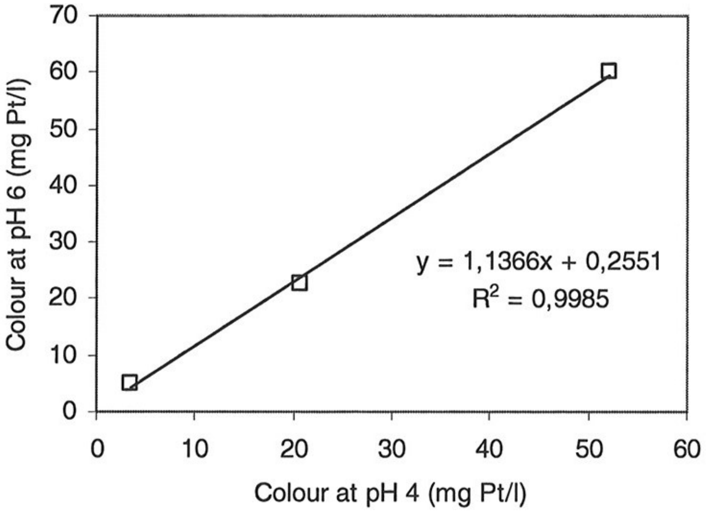


Figure A - 1. True colour (< 0,45 μm) measured at pH 6 plotted as function of colour measured at pH 4 in the same samples. The coefficients and factor in the equation describing the suggested regression line (generated in Microsoft Excel) carry to many significant numbers, but this was allowed for in order not to have the regressional coefficient (R^2) take the value of 1,00.

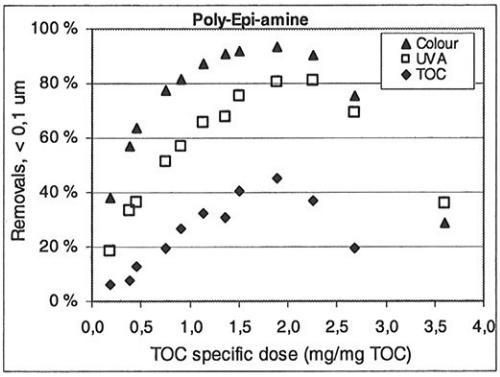
In direct comparisons between experiments performed at pH 4 and pH 6, the colour measurements obtained at pH 4 have been corrected to corresponding values at pH 6 using the regression equation in figure I. The true relationship between colour at pH 6 and pH 4 at different concentrations as expressed in the regression in figure I is not linear, but the error resulting from the deviation from linearity was considered to be small enough in the relevant pH- and concentration ranges that a linear relationship could be applied in the correction of colour values from pH 4 to 6.

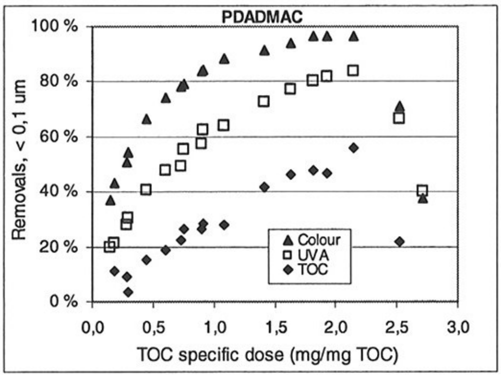
An analogue approach was attempted for pH-correction of UV-absorbance measurements. However, in the pH- and concentrations ranges encountered in this work the differences in UVA-values at pH 6 and 4 were found to be negligible (< 1%).

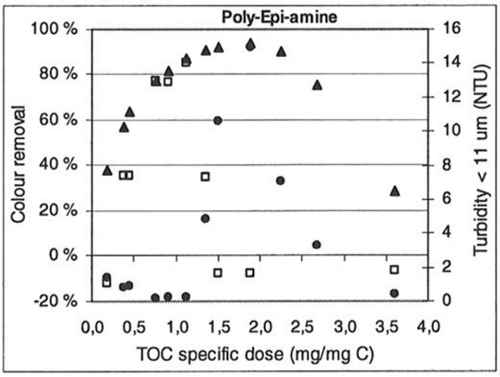
APPENDIX - D

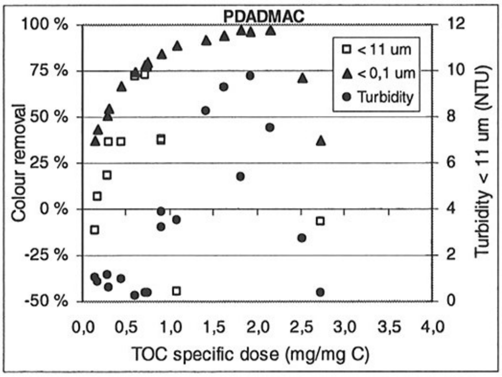
The following graphic presentations have been included in this appendix in order to verify statements, generally with regards to similarities in the performances of different polyelectrolytes, made in the main part of the thesis.

Similarity between the performances of PDADMAC and poly-Epi-amine with respect to coagulation of coloured substances, UV-absorbing substances and TOC (with reference to upper left parts of figures 5.4 and 5.6 and interpretations of these).

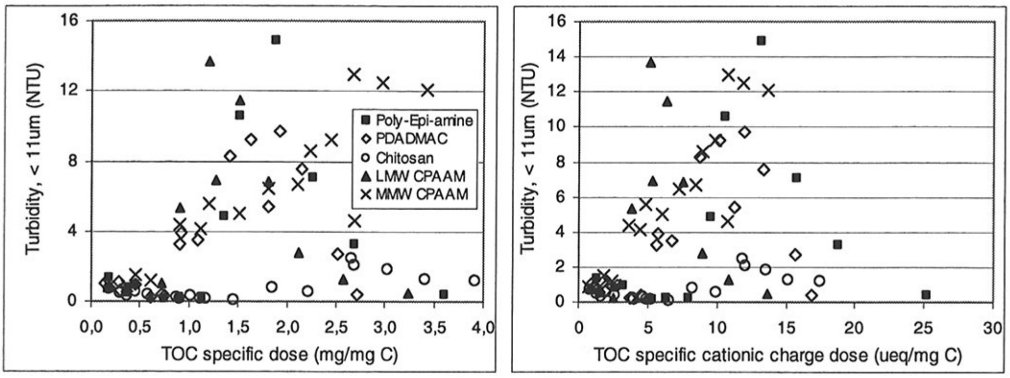




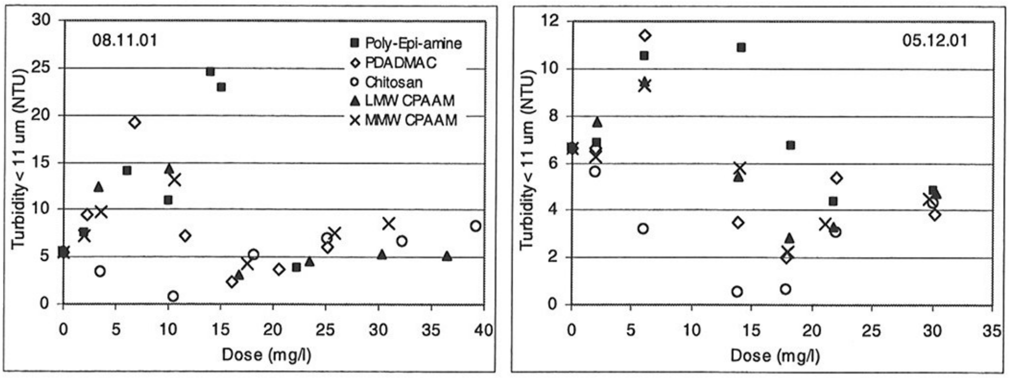




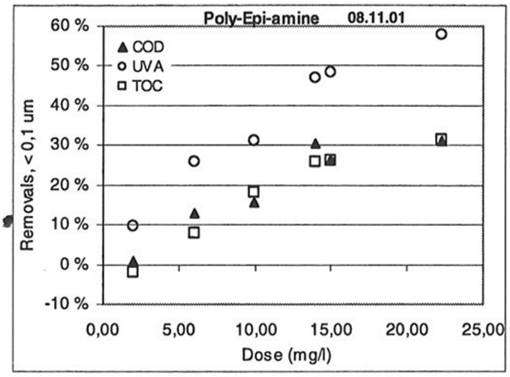
Turbidity (humic water) measured after filtration through 11 μm paper filter for all polyelectrolytes (with reference to lower left parts of figures 5.7 and 5.8 and interpretations of these).

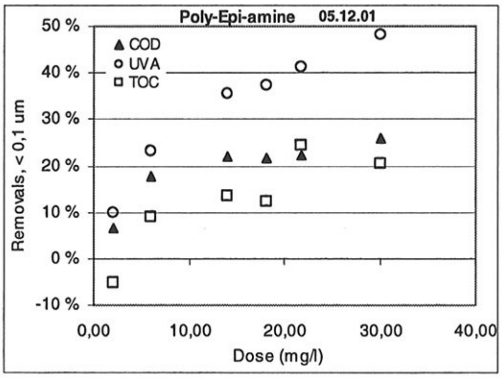


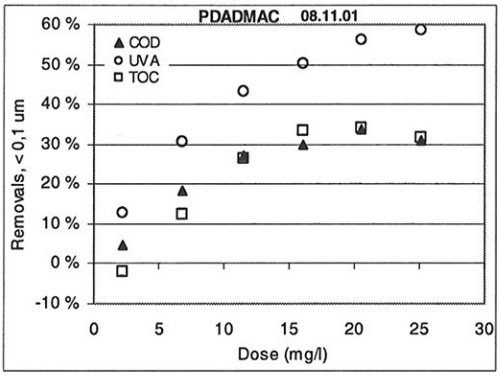
Turbidity (wastewater) measured after filtration through 11 μm paper filter for all polyelectrolytes (with reference to figure 6.2 and interpretation of this).

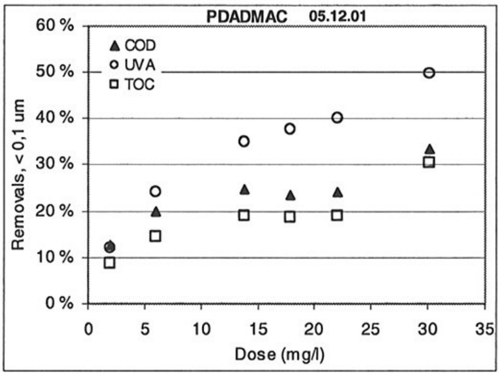


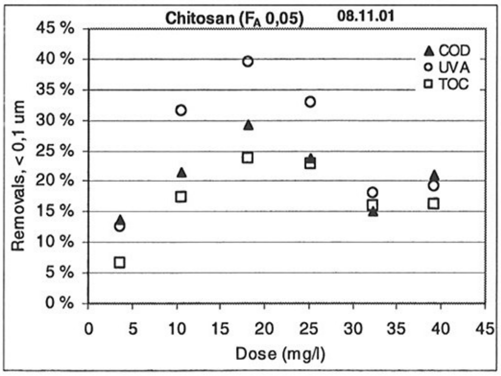
Comparison of dosage responses with respect to UVA, COD and TOC for all polyelectrolytes tested (with reference to figure 6.3 and interpretation of this).

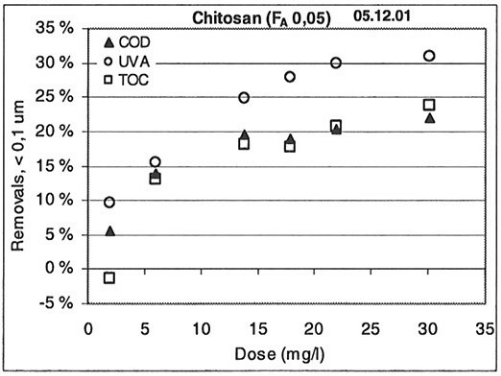


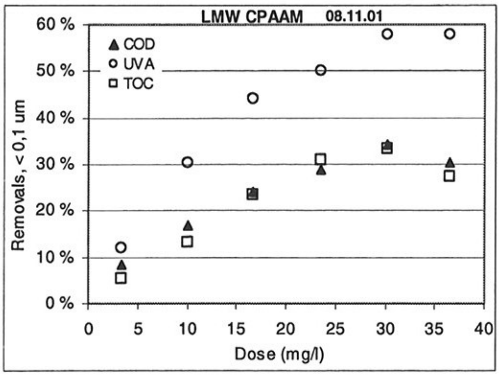


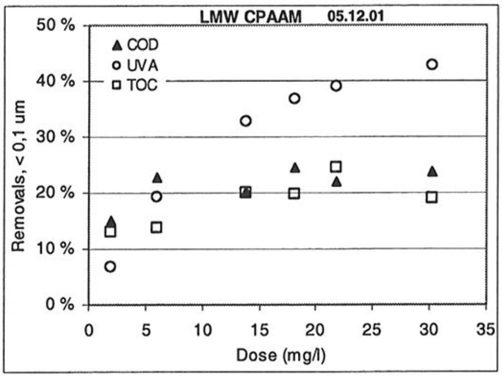


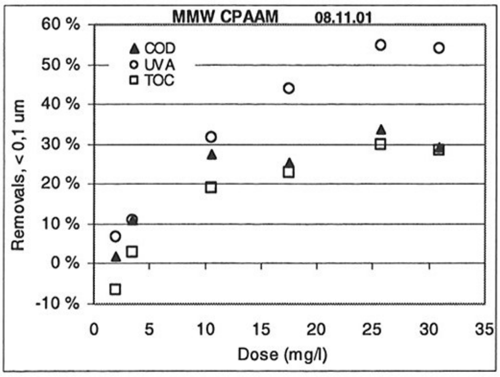


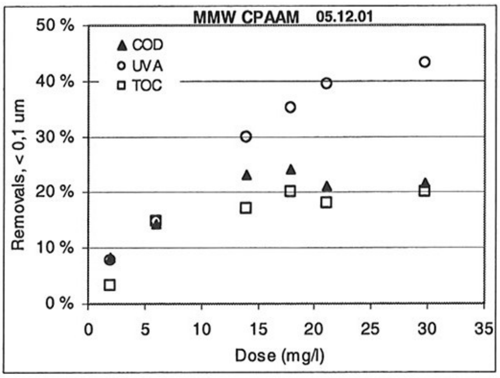




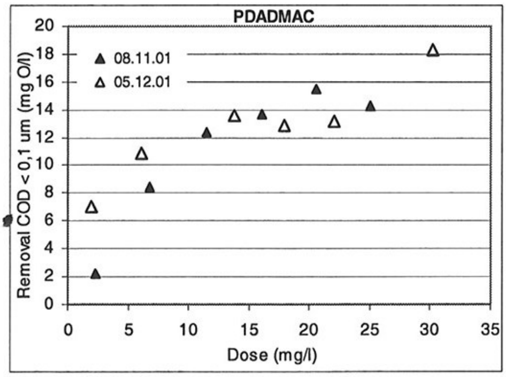

LMW CPAAM 08.11.01
▲ COD
○ UVA
□ TOC
Removals, < 0,1 um
0 %
10 %
20 %
30 %
40 %
50 %
60 %
0
5
10
15
20
25
30
35
40
Dose (mg/l)

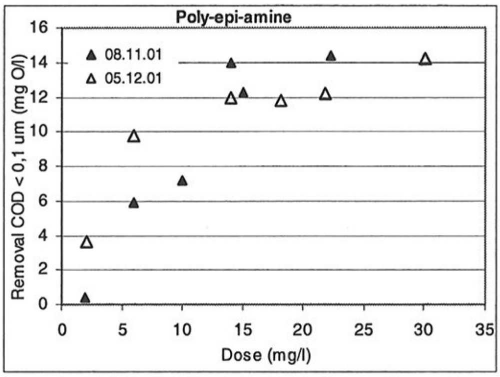

LMW CPAAM 05.12.01
▲ COD
○ UVA
□ TOC
Removals, < 0,1 um
0 %
10 %
20 %
30 %
40 %
50 %
0
5
10
15
20
25
30
35
Dose (mg/l)

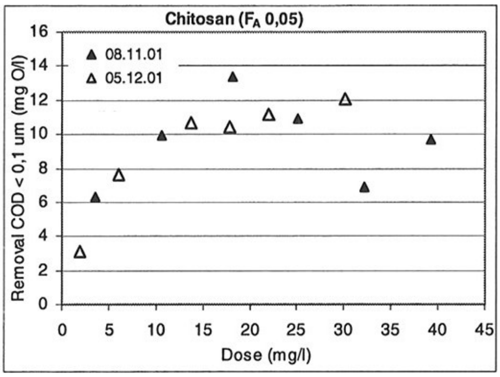

MMW CPAAM 08.11.01
▲ COD
○ UVA
□ TOC
Removals, < 0,1 um
-10 %
0 %
10 %
20 %
30 %
40 %
50 %
60 %
0
5
10
15
20
25
30
35
Dose (mg/l)

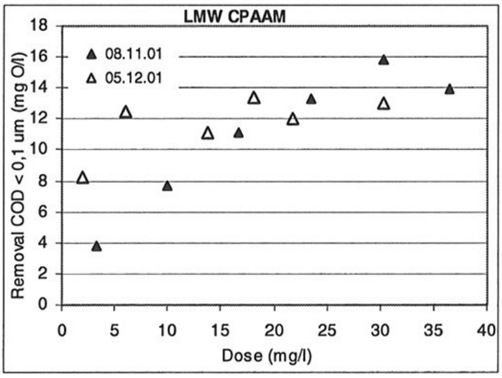

MMW CPAAM 05.12.01
▲ COD
○ UVA
□ TOC
Removals, < 0,1 um
0 %
10 %
20 %
30 %
40 %
50 %
0
5
10
15
20
25
30
35
Dose (mg/l)

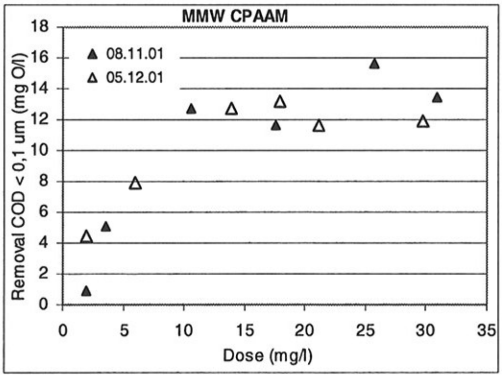
Effect of differences in raw water COD concentrations and distributions for all polyelectrolytes tested (with reference to figure 6.4 and interpretation of this).











APPENDIX - E

Raw data from experiments on humic water

Chitosan

Coagulant: Chitosan $F_A = 0,05$
pH : 4,0 +/- 0,1
Date: 05-sep-01

Dosage							
mg/l	0,0	2,0	4,0	5,0	6,0	8,0	10,0
mg/mg C	Raw-	0,3	0,6	0,8	0,9	1,2	1,5
ueq/mg C	water	1,7	3,4	4,2	5,1	6,7	8,4
Analysis results							
Turb. < 11 um (NTU)	0,25	0,21	0,21	0,47	1,34	0,39	0,30
Col. < 11 um (mg Pt/l)	47,1	25,1	16,1	19,6	37,6	45,1	45,5
Col. < 11 um (pH 6)*	53,8	28,8	18,5	22,5	43,0	51,5	51,9
Col. < 1,2 um (mg Pt/l)	47,1	22,9	14,1	11,4	9,9	40,5	43,1
Col. < 0,45 um (mg Pt/l)	44,3	22,6	13,6	11,1	9,5	33,5	40,4
Col. < 0,1 um (mg Pt/l)	44,3	21,7	13,7	11,4	9,5	6,3	4,8
Col. < 0,1 um (pH 6)*	50,6	24,9	15,8	13,2	11,0	7,4	5,8
UVA < 11 um (m^{-1})	30,4	22,7	18,0	18,2	25,0	27,4	27,9
UVA < 1,2 um (m^{-1})	30,8	22,9	18,1	16,4	15,2	26,2	27,3
UVA < 0,45 um (m^{-1})	31,2	23,1	18,3	16,9	15,5	23,5	26,4
UVA < 0,1 um (m^{-1})	31,2	22,7	18,4	17,0	15,5	12,5	10,8
TOC < 11 um (mg C/l)	6,6	5,7	5,1	5,4	7,4	9,0	9,8
TOC < 1,2 um (mg C/l)	6,7	5,7	5,0	4,7	4,5	8,5	9,3
TOC < 0,45 um (mg C/l)	6,7	5,6	4,8	4,5	4,3	7,2	8,9
TOC < 0,1 um (mg C/l)	6,8	6,2	5,0	4,9	4,8	4,8	3,8
Calculated removal results							
Col. < 11 um		47 %	66 %	58 %	20 %	4 %	3 %
Col. < 11 um (pH 6)*		47 %	66 %	58 %	20 %	4 %	3 %
Col. < 1,2 um		51 %	70 %	76 %	79 %	14 %	8 %
Col. < 0,45 um		49 %	69 %	75 %	79 %	24 %	9 %
Col. < 0,1 um		51 %	69 %	74 %	79 %	86 %	89 %
Col. < 0,1 um (pH 6)*		51 %	69 %	74 %	78 %	85 %	89 %
UVA < 11 um		25 %	41 %	40 %	18 %	10 %	8 %
UVA < 1,2 um		26 %	41 %	47 %	51 %	15 %	12 %
UVA < 0,45 um		26 %	41 %	46 %	50 %	25 %	16 %
UVA < 0,1 um		27 %	41 %	46 %	50 %	60 %	65 %
TOC < 11 um		14 %	22 %	19 %	-12 %	-37 %	-49 %
TOC < 1,2 um							
TOC < 0,45 um		16 %	28 %	33 %	36 %	-8 %	-32 %
TOC < 0,1 um		9 %	26 %	28 %	30 %	29 %	45 %

* Values corrected to pH 6 according to protocol given in appendix C

Coagulant: Chitosan $F_A = 0,05$
pH : 6,0 +/- 0,1
Date: 5-sep-2001

Dosage							
mg/l	0,00	2,0	4,1	6,1	7,2	8,2	10,2
mg/mg C	Raw-	0,3	0,6	0,9	1,0	1,2	1,5
ueq/mg C	water	1,3	2,6	3,9	4,6	5,2	6,5
Analysis results							
Turb. < 11 um (NTU)	0,16	0,51	0,37	0,21	0,35	0,17	0,11
Col. < 11 um (mg Pt/l)	56,3	41,4	26,1	15,7	15,2	10,2	7,2
Col. < 1,2 um (mg Pt/l)	55,6	32,0	20,4	14,2	12,5	10,0	7,4
Col. < 0,45 um (mg Pt/l)	54,8	30,7	20,1	14,1	12,4	9,8	7,4
Col. < 0,1 um (mg Pt/l)	52,8	30,3	20,4	14,3	12,3	9,9	7,6
UVA < 11 um (m^{-1})	32,7	26,5	21,5	16,8	16,2	13,6	11,2
UVA < 1,2 um (m^{-1})	32,9	25,3	20,6	17,3	15,7	14,0	11,4
UVA < 0,45 um (m^{-1})	33,0	25,5	20,8	16,9	16,0	14,1	11,8
UVA < 0,1 um (m^{-1})	32,5	25,3	20,9	17,5	16,2	14,2	12,0
TOC < 11 um (mg C/l)	7,0	6,4	5,8	4,8	4,8	4,3	3,8
TOC < 1,2 um (mg C/l)	7,1	6,2	5,5	5,0	4,7	4,3	3,9
TOC < 0,45 um (mg C/l)	7,1	6,0	5,4	4,7	4,5	4,1	3,7
TOC < 0,1 um (mg C/l)	6,8	6,2	5,0	4,9	4,8	4,8	3,8
Calculated removal results							
Col. < 11 um		27 %	54 %	72 %	73 %	82 %	87 %
Col. < 1,2 um		42 %	63 %	74 %	77 %	82 %	87 %
Col. < 0,45 um		44 %	63 %	74 %	77 %	82 %	87 %
Col. < 0,1 um		43 %	61 %	73 %	77 %	81 %	86 %
UVA < 11 um		19 %	34 %	49 %	50 %	58 %	66 %
UVA < 1,2 um		23 %	37 %	47 %	52 %	57 %	65 %
UVA < 0,45 um		23 %	37 %	49 %	51 %	57 %	64 %
UVA < 0,1 um		22 %	36 %	46 %	50 %	56 %	63 %
TOC < 11 um		8 %	17 %	31 %	31 %	39 %	46 %
TOC < 1,2 um		13 %	22 %	29 %	34 %	40 %	45 %
TOC < 0,45 um		16 %	24 %	33 %	37 %	42 %	48 %
TOC < 0,1 um		16 %	23 %	31 %	35 %	39 %	45 %

Coagulant: Chitosan $F_A = 0,05$
pH : 6,0 +/- 0,1
Date: 25-sep-2001

Dosage							
mg/l	0,0	1,0	2,0	5,0	6,1	10,2	14,8
mg/mg C	Raw-	0,2	0,4	0,9	1,1	1,9	2,7
ueq/mg C	water	0,8	1,7	4,1	5,0	8,3	12,0
Analysis results							
Turb. < 11 um (NTU)	0,34	0,72	0,34	0,20	0,19	0,78	2,10
Col. < 11 um (mg Pt/l)	48,6	47,0	30,5	15,9	13,6	14,2	51,2
Col. < 1,2 um (mg Pt/l)	47,7	36,3	23,9	13,4	10,8	5,8	44,4
Col. < 0,45 um (mg Pt/l)	45,3	29,8	22,8	13,0	10,3	5,4	38,2
Col. < 0,1 um (mg Pt/l)	43,8	28,0	22,2	12,4	9,8	4,9	2,6
UVA < 11 um (m^{-1})	26,3	24,7	20,5	14,5	12,7	10,2	24,9
UVA < 1,2 um (m^{-1})	26,5	23,0	19,1	14,1	12,3	7,9	22,9
UVA < 0,45 um (m^{-1})	26,2	21,3	19,4	14,1	12,3	8,3	20,7
UVA < 0,1 um (m^{-1})	25,4	20,6	18,8	13,8	12,1	7,9	5,8
TOC < 11 um (mg C/l)	5,5	5,2	4,7	4,2	3,8	4,4	11,2
TOC < 1,2 um (mg C/l)	5,4	5,3	4,9	4,3	4,6	3,5	10,2
TOC < 0,45 um (mg C/l)	5,7	5,4	5,2	4,8	4,4	3,6	9,8
TOC < 0,1 um (mg C/l)	6,1	5,3	5,1	4,7	4,5	3,8	3,2
Calculated removal results							
Col. < 11 um		3 %	37 %	67 %	72 %	71 %	-5 %
Col. < 1,2 um		24 %	50 %	72 %	77 %	88 %	7 %
Col. < 0,45 um		34 %	50 %	71 %	77 %	88 %	16 %
Col. < 0,1 um		36 %	49 %	72 %	78 %	89 %	94 %
UVA < 11 um		6 %	22 %	45 %	52 %	61 %	6 %
UVA < 1,2 um		13 %	28 %	47 %	54 %	70 %	14 %
UVA < 0,45 um		19 %	26 %	46 %	53 %	68 %	21 %
UVA < 0,1 um		19 %	26 %	46 %	53 %	69 %	77 %
TOC < 11 um		7 %	14 %	24 %	30 %	20 %	-103 %
TOC < 1,2 um		1 %	8 %	19 %	15 %	36 %	-89 %
TOC < 0,45 um		5 %	7 %	15 %	22 %	36 %	-73 %
TOC < 0,1 um		13 %	17 %	22 %	27 %	37 %	48 %

Coagulant: Chitosan $F_A = 0,05$
pH : 6,0 +/- 0,1
Date: 26-nov-2001

Dosage							
mg/l	0,0	3,1	15,2	18,2	20,7	23,2	26,8
mg/mg C	Raw-	0,5	2,2	2,7	3,0	3,4	3,9
ueq/mg C	water	2,0	9,9	11,9	13,5	15,2	17,5
Analysis results							
Turb. < 11 um (NTU)	0,14	0,56	0,58	2,49	1,83	1,30	1,23
Col. < 11 um (mg Pt/l)	63,4	39,2	11,2	68,9	66,2	68,2	68,9
Col. < 1,2 um (mg Pt/l)	62,3	29,7	6,4	60,2	56,8	62,7	63,4
Col. < 0,45 um (mg Pt/l)	60,2	26,6	5,6	32,8	46,8	60,2	61,6
Col. < 0,1 um (mg Pt/l)	58,2	26,0	5,6	3,1	3,3	2,3	2,1
UVA < 11 um (m^{-1})	33,1	24,9	9,4	30,4	32,0	32,4	25,9
UVA < 1,2 um (m^{-1})	34,4	23,5	9,2	28,5	28,6	31,7	32,1
UVA < 0,45 um (m^{-1})	35,0	23,1	9,4	19,6	25,7	31,6	32,3
UVA < 0,1 um (m^{-1})	33,1	23,3	9,6	7,5	7,6	6,9	6,3
TOC < 11 um (mg C/l)	6,8	5,6	4,2	13,2	14,2	16,7	18,1
TOC < 1,2 um (mg C/l)	6,9	6,2	4,0	12,2	12,7	16,2	17,3
TOC < 0,45 um (mg C/l)	7,4	6,3	3,9	8,1	11,3	15,6	17,4
TOC < 0,1 um (mg C/l)	7,1	6,5	4,2	4,2	4,5	4,9	4,6
Calculated removal results							
Col. < 11 um		38 %	82 %	-9 %	-5 %	-8 %	-9 %
Col. < 1,2 um		52 %	90 %	3 %	9 %	-1 %	-2 %
Col. < 0,45 um		56 %	91 %	46 %	22 %	0 %	-2 %
Col. < 0,1 um		55 %	90 %	95 %	94 %	96 %	96 %
UVA < 11 um		25 %	71 %	8 %	3 %	2 %	22 %
UVA < 1,2 um		32 %	73 %	17 %	17 %	8 %	7 %
UVA < 0,45 um		34 %	73 %	44 %	27 %	10 %	8 %
UVA < 0,1 um		29 %	71 %	77 %	77 %	79 %	81 %
TOC < 11 um		18 %	38 %	-93 %	-107 %	-145 %	-165 %
TOC < 1,2 um		11 %	42 %	-76 %	-83 %	-133 %	-149 %
TOC < 0,45 um		14 %	48 %	-10 %	-54 %	-111 %	-136 %
TOC < 0,1 um		8 %	40 %	41 %	37 %	31 %	35 %

Coagulant: Chitosan $F_A = 0,37$
pH : 4,0 +/- 0,1
Date: 19-des-2001

Dosage							
mg/l	0,0	3,4	6,8	8,5	10,2	13,8	16,8
mg/mg C	Raw-	0,5	1,0	1,2	1,5	2,0	2,4
ueq/mg C	water	1,5	3,0	3,7	4,5	6,0	7,4
Analysis results							
Turb. < 11 um (NTU)	0,13	0,20	1,45	0,88	0,54	0,45	0,38
Col. < 11 um (mg Pt/l)	52,4	29,3	54,7	49,3	51,1	54,0	55,1
Col. < 11 um (pH 6)*		33,6	62,4	56,3	58,3	61,6	62,9
Col. < 1,2 um (mg Pt/l)							
Col. < 0,45 um (mg Pt/l)	49,8	25,7	16,6	18,4	33,8	45,0	47,9
Col. < 0,1 um (mg Pt/l)	46,3	24,7	16,3	12,9	11,1	7,9	8,5
Col. < 0,1 um (pH 6)*		28,3	18,8	14,9	12,9	9,3	9,9
UVA < 11 um (m^{-1})	32,6	25,2	27,1	29,8	30,6	31,3	31,8
UVA < 1,2 um (m^{-1})							
UVA < 0,45 um (m^{-1})	32,5	24,8	20,1	19,4	24,0	28,5	29,7
UVA < 0,1 um (m^{-1})	31,1	24,3	20,0	17,8	16,4	13,8	12,9
TOC < 11 um (mg C/l)	7,0	6,3	8,2	8,5	9,5	10,9	12,2
TOC < 1,2 um (mg C/l)							
TOC < 0,45 um (mg C/l)	6,9	6,1	5,5	5,5	7,3	9,6	11,1
TOC < 0,1 um (mg C/l)	7,2	6,8	6,5	5,6	6,1	6,1	5,9
Calculated removal results							
Col. < 11 um		53 %	12 %	21 %	18 %	13 %	11 %
Col. < 11 um (pH 6)**		46 %	-1 %	9 %	6 %	1 %	-1 %
Col. < 1,2 um							
Col. < 0,45 um		58 %	73 %	70 %	45 %	27 %	22 %
Col. < 0,1 um		59 %	73 %	79 %	82 %	87 %	86 %
Col. < 0,1 um (pH 6)**		53 %	69 %	75 %	79 %	85 %	84 %
UVA < 11 um		26 %	20 %	12 %	10 %	8 %	7 %
UVA < 1,2 um							
UVA < 0,45 um		27 %	41 %	43 %	30 %	16 %	13 %
UVA < 0,1 um		29 %	41 %	48 %	52 %	59 %	62 %
TOC < 11 um		9 %	-18 %	-22 %	-36 %	-57 %	-76 %
TOC < 1,2 um							
TOC < 0,45 um		11 %	20 %	20 %	-7 %	-40 %	-61 %
TOC < 0,1 um		5 %	10 %	22 %	15 %	15 %	18 %

* Values corrected to pH 6 according to protocol given in appendix C

** Removals calulated relative to values actually measured in raw water at pH 6 (below)

Coagulant: Chitosan F_A = 0,37
pH : 6,0 +/- 0,1
Date: 19-des-2001

Dosage							
mg/l	0,0	5,5	10,7	16,3	20,4	24,5	28,5
mg/mg C	Raw-	0,8	1,5	2,3	2,9	3,5	4,1
ueq/mg C	water	1,9	3,8	5,7	7,2	8,6	10,0
Analysis results							
Turb. < 11 um (NTU)	0,14	0,20	0,11	3,05	1,98	1,76	1,17
Col. < 11 um (mg Pt/l)	62,1	30,5	17,1	65,6	61,6	62,4	64,8
Col. < 1,2 um (mg Pt/l)							
Col. < 0,45 um (mg Pt/l)	61,4	27,7	16,1	10,4	23,7	46,4	55,6
Col. < 0,1 um (mg Pt/l)	60,2	27,8	16,4	10,4	8,2	6,8	5,5
UVA < 11 um (m^{-1})	34,1	23,6	17,7	20,2	30,5	31,3	32,8
UVA < 1,2 um (m^{-1})							
UVA < 0,45 um (m^{-1})	34,0	23,4	17,9	14,1	16,7	25,5	29,7
UVA < 0,1 um (m^{-1})	34,0	24,0	18,4	14,7	12,8	12,3	10,1
TOC < 11 um (mg C/l)	7,0	5,8	5,3	9,9	12,1	13,9	15,5
TOC < 1,2 um (mg C/l)							
TOC < 0,45 um (mg C/l)	6,9	6,0	5,3	5,5	6,0	10,7	13,7
TOC < 0,1 um (mg C/l)	7,2	6,3	5,8	6,0	7,1	8,9	7,1
Calculated removal results							
Col. < 11 um		51 %	72 %	-6 %	1 %	-1 %	-4 %
Col. < 1,2 um							
Col. < 0,45 um		55 %	74 %	83 %	61 %	24 %	9 %
Col. < 0,1 um		54 %	73 %	83 %	86 %	89 %	91 %
UVA < 11 um		31 %	48 %	41 %	11 %	8 %	4 %
UVA < 1,2 um							
UVA < 0,45 um		31 %	47 %	58 %	51 %	25 %	13 %
UVA < 0,1 um		29 %	46 %	57 %	62 %	64 %	70 %
TOC < 11 um		17 %	24 %	-42 %	-74 %	-100 %	-123 %
TOC < 1,2 um							
TOC < 0,45 um		13 %	23 %	21 %	12 %	-55 %	-100 %
TOC < 0,1 um		12 %	19 %	17 %	1 %	-24 %	2 %

PDADMAC

Coagulant: PDADMAC (Cytec C-591)
pH : 6,0 +/- 0,1
Date: 15-sep-01

Dosage							
mg/l	0,0	1,0	2,0	3,0	4,0	5,0	6,1
mg/mg C	Raw-	0,1	0,3	0,5	0,6	0,8	0,9
ueq/mg C	water	0,9	1,9	2,8	3,7	4,7	5,7
Analysis results							
Turb. < 11 um (NTU)	0,17	1,01	0,60	0,96	0,23	0,34	3,87
Col. < 11 um (mg Pt/l)	59,3	66,2	37,9	37,8	16,6	13,9	37,2
Col. < 1,2 um (mg Pt/l)	55,1	50,1	26,3	18,6	14,7	11,5	8,8
Col. < 0,45 um (mg Pt/l)	55,6	40,8	24,7	18,3	14,2	11,1	8,2
Col. < 0,1 um (mg Pt/l)	53,7	33,7	24,4	18,0	13,9	11,1	8,4
UVA < 11 um (m^{-1})	31,1	32,0	23,0	21,2	15,6	13,6	13,4
UVA < 1,2 um (m^{-1})	30,7	28,5	21,0	18,1	15,9	13,5	11,3
UVA < 0,45 um (m^{-1})	30,2	25,7	20,7	17,8	15,8	13,5	11,7
UVA < 0,1 um (m^{-1})	29,8	23,9	20,7	17,8	15,6	13,3	11,3
TOC < 11 um (mg C/l)	6,6	7,3	6,3	6,1	5,1	4,6	4,6
TOC < 1,2 um (mg C/l)	7,2	7,3	6,1	5,7	5,3	4,9	4,5
TOC < 0,45 um (mg C/l)	6,6	6,5	6,0	5,7	5,3	5,0	4,6
TOC < 0,1 um (mg C/l)	7,0	7,8	6,7	5,9	5,7	5,2	5,0
Calculated removal results							
Col. < 11 um		-12 %	36 %	36 %	72 %	77 %	37 %
Col. < 1,2 um		9 %	52 %	66 %	73 %	79 %	84 %
Col. < 0,45 um		27 %	56 %	67 %	75 %	80 %	85 %
Col. < 0,1 um		37 %	55 %	66 %	74 %	79 %	84 %
UVA < 11 um		-3 %	26 %	32 %	50 %	56 %	57 %
UVA < 1,2 um		7 %	32 %	41 %	48 %	56 %	63 %
UVA < 0,45 um		15 %	31 %	41 %	48 %	55 %	61 %
UVA < 0,1 um		20 %	31 %	40 %	48 %	55 %	62 %
TOC < 11 um		-10 %	5 %	8 %	23 %	30 %	31 %
TOC < 1,2 um		-1 %	15 %	20 %	27 %	32 %	38 %
TOC < 0,45 um		1 %	9 %	14 %	19 %	25 %	30 %
TOC < 0,1 um		-11 %	4 %	15 %	19 %	26 %	28 %

Coagulant: PDADMAC (Cytec C-591)
pH : 6,0 +/- 0,1
Date: 25-sep-01

Dosage							
mg/l	0,00	1,0	4,0	5,0	6,0	10,0	15,0
mg/mg C	Raw-	0,2	0,7	0,9	1,1	1,8	2,7
ueq/mg C	water	1,1	4,5	5,6	6,7	11,2	16,8
Analysis results							
Turb. < 11 um (NTU)	0,34	0,82	0,36	3,23	3,49	5,41	0,39
Col. < 11 um (mg Pt/l)	48,6	45,1	13,3	30,2	70,4	134,9	52,0
Col. < 1,2 um (mg Pt/l)	47,7	28,9	10,7	8,0	5,8	6,9	48,6
Col. < 0,45 um (mg Pt/l)	45,3	25,4	10,0	7,1	5,4	3,3	47,8
Col. < 0,1 um (mg Pt/l)	43,8	25,0	9,5	7,0	5,0	1,5	27,4
UVA < 11 um (m^{-1})	26,3	23,5	13,0	12,7	11,9	10,9	24,9
UVA < 1,2 um (m^{-1})	26,5	21,0	13,2	10,7	9,0	6,6	24,4
UVA < 0,45 um (m^{-1})	26,2	19,6	12,5	10,8	9,0	5,7	23,7
UVA < 0,1 um (m^{-1})	25,4	20,0	12,9	10,8	9,1	5,0	15,2
TOC < 11 um (mg C/l)	5,5	5,5	4,3	4,0	4,5	7,1	13,3
TOC < 1,2 um (mg C/l)	5,4	5,3	4,4	3,9	3,6	3,1	13,6
TOC < 0,45 um (mg C/l)	5,7	5,5	4,6	4,2	3,8	3,3	12,8
TOC < 0,1 um (mg C/l)	6,1	5,4	4,7	4,5	4,4	3,2	9,0
Calculated removal results							
Col. < 11 um		7 %	73 %	38 %	-45 %	-178 %	-7 %
Col. < 1,2 um		39 %	78 %	83 %	88 %	85 %	-2 %
Col. < 0,45 um		44 %	78 %	84 %	88 %	93 %	-5 %
Col. < 0,1 um		43 %	78 %	84 %	89 %	97 %	38 %
UVA < 11 um		11 %	51 %	52 %	55 %	59 %	5 %
UVA < 1,2 um		21 %	50 %	60 %	66 %	75 %	8 %
UVA < 0,45 um		25 %	52 %	59 %	66 %	78 %	10 %
UVA < 0,1 um		21 %	49 %	58 %	64 %	80 %	40 %
TOC < 11 um		0 %	23 %	28 %	19 %	-28 %	-141 %
TOC < 1,2 um		1 %	19 %	27 %	33 %	43 %	-152 %
TOC < 0,45 um		3 %	19 %	26 %	33 %	42 %	-127 %
TOC < 0,1 um		11 %	22 %	26 %	28 %	48 %	-47 %

Coagulant:	PDADMAC (Cytec C-591)
pH :	6,0 +/- 0,1
Date:	26-nov-2001

Dosage							
mg/l	0,0	1,9	9,7	11,1	13,2	14,7	17,2
mg/mg C	Raw-	0,3	1,4	1,6	1,9	2,1	2,5
ueq/mg C	water	1,8	8,8	10,1	11,9	13,3	15,6
Analysis results							
Turb. < 11 um (NTU)	0,14	1,15	8,24	9,26	9,73	7,54	2,73
Col. < 11 um (mg Pt/l)	63,4	51,7	142,3				
Col. < 1,2 um (mg Pt/l)	62,3	35,3	6,0	5,9	9,4	14,3	44,6
Col. < 0,45 um (mg Pt/l)	60,2	28,5	4,7	3,7	4,2	7,1	41,4
Col. < 0,1 um (mg Pt/l)	58,2	28,8	4,9	3,6	2,2	2,0	17,0
UVA < 11 um (m^{-1})	33,1	27,4	16,6	15,2	14,4	29,0	
UVA < 1,2 um (m^{-1})	34,4	25,8	9,9	8,9	8,8	9,8	23,5
UVA < 0,45 um (m^{-1})	35,0	23,9	8,6	7,5	6,5	7,5	22,6
UVA < 0,1 um (m^{-1})	33,1	23,9	9,1	7,6	6,1	5,5	11,1
TOC < 11 um (mg C/l)	6,8	6,2	5,9	7,6	10,7	11,4	12,4
TOC < 1,2 um (mg C/l)	6,9	6,9	4,0	3,6	3,5	4,4	11,3
TOC < 0,45 um (mg C/l)	7,4	6,4	4,3	3,5	3,2	3,9	10,7
TOC < 0,1 um (mg C/l)	7,1	6,4	4,1	3,8	3,8	3,1	5,5
Calculated removal results							
Col. < 11 um		18 %	-125 %				
Col. < 1,2 um		43 %	90 %	91 %	85 %	77 %	28 %
Col. < 0,45 um		53 %	92 %	94 %	93 %	88 %	31 %
Col. < 0,1 um		51 %	92 %	94 %	96 %	97 %	71 %
UVA < 11 um		17 %	50 %	54 %	57 %	12 %	
UVA < 1,2 um		25 %	71 %	74 %	74 %	71 %	32 %
UVA < 0,45 um		32 %	75 %	78 %	81 %	78 %	35 %
UVA < 0,1 um		28 %	72 %	77 %	82 %	84 %	66 %
TOC < 11 um		9 %	14 %	-11 %	-57 %	-67 %	-81 %
TOC < 1,2 um		1 %	42 %	48 %	49 %	36 %	-62 %
TOC < 0,45 um		13 %	42 %	52 %	57 %	47 %	-46 %
TOC < 0,1 um		9 %	41 %	46 %	47 %	56 %	22 %

Coagulant:	PDADMAC (Cytec C-591)					
pH :	4,0 +/- 0,1					
Date:	19-des-2001					
Dosage						
mg/l	0,0	2,0	4,0	5,0	6,7	10,3
mg/mg C	Raw-	0,3	0,6	0,7	1,0	1,5
ueq/mg C	water	1,8	3,6	4,5	5,9	9,1
Analysis results						
Turb. < 11 um (NTU)	0,13	0,55	0,20	1,16	2,33	0,50
Col. < 11 um (mg Pt/l)	52,4	35,4	11,8	28,2	62,0	55,2
Col. < 11 um (pH 6)*		40,5	13,6	32,3	70,7	63,0
Col. < 1,2 um (mg Pt/l)						
Col. < 0,45 um (mg Pt/l)	49,8	19,2	9,6	7,9	6,3	46,6
Col. < 0,1 um (mg Pt/l)	46,3	18,9	9,4	7,8	5,4	19,2
Col. < 0,1 um (pH 6)*		21,7	10,9	9,1	6,3	22,1
UVA < 11 um (m^{-1})	32,6	23,9	14,5	16,8	26,7	29,9
UVA < 1,2 um (m^{-1})						
UVA < 0,45 um (m^{-1})	32,5	21,8	15,2	14,0	11,5	28,5
UVA < 0,1 um (m^{-1})	31,1	21,1	14,5	13,3	10,6	13,5
TOC < 11 um (mg C/l)	7,0	6,6	4,8	5,6	7,4	11,3
TOC < 1,2 um (mg C/l)						
TOC < 0,45 um (mg C/l)	6,9	5,7	4,7	4,6	4,0	11,3
TOC < 0,1 um (mg C/l)	7,2	6,3	5,0	4,9	4,5	5,6
Calculated removal results						
Col. < 11 um		32 %	78 %	46 %	-18 %	-5 %
Col. < 11 um (pH 6)**		35 %	78 %	48 %	-14 %	-2 %
Col. < 1,2 um						
Col. < 0,45 um		62 %	81 %	84 %	87 %	6 %
Col. < 0,1 um		59 %	80 %	83 %	88 %	59 %
Col. < 0,1 um (pH 6)**		64 %	82 %	85 %	89 %	63 %
UVA < 11 um		27 %	55 %	48 %	18 %	8 %
UVA < 1,2 um						
UVA < 0,45 um		33 %	53 %	57 %	65 %	12 %
UVA < 0,1 um		32 %	53 %	57 %	66 %	57 %
TOC < 11 um		5 %	31 %	20 %	-6 %	-63 %
TOC < 1,2 um						
TOC < 0,45 um		17 %	32 %	34 %	42 %	-64 %
TOC < 0,1 um		13 %	30 %	32 %	38 %	22 %

* Values corrected to pH 6 according to protocol given in appendix C

** Removals calulated relative to values actually measured in raw water at pH 6 (chitosan F_A = 0,37, 19. Dec.01)

Poly-Epi-amine

Coagulant: Poly-Epi-amine (Cytec C-581)
pH : 6,0 +/- 0,1
Date: 15-sep-01

Dosage							
mg/l	0,0	2,5	5,0	7,5	10,0	12,5	15,0
mg/mg C	Raw-	0,4	0,8	1,1	1,5	1,9	2,3
ueq/mg C	water	2,6	5,3	7,9	10,6	13,2	15,8
Analysis results							
Turb. < 11 um (NTU)	0,17	0,80	0,15	0,21	10,60	14,90	7,08
Col. < 11 um (mg Pt/l)	59,3	38,2	13,5	8,8	63,8	63,7	74,6
Col. < 1,2 um (mg Pt/l)	55,1	23,2	12,6	7,3	5,3	5,7	31,2
Col. < 0,45 um (mg Pt/l)	55,6	23,2	12,3	7,2	4,9	5,1	27,5
Col. < 0,1 um (mg Pt/l)	53,7	23,2	12,1	6,9	4,4	3,5	5,1
UVA < 11 um (m^{-1})	31,1	22,7	14,1	9,9	12,1	11,7	17,3
UVA < 1,2 um (m^{-1})	30,7	20,1	14,2	10,1	7,6	7,4	15,4
UVA < 0,45 um (m^{-1})	30,2	19,7	14,1	9,5	7,2	6,6	14,4
UVA < 0,1 um (m^{-1})	29,8	19,9	14,5	10,3	7,4	5,9	5,7
TOC < 11 um (mg C/l)	6,6	6,2	5,0	4,2	5,1	7,1	9,6
TOC < 1,2 um (mg C/l)	7,2	6,1	5,3	4,4	4,2	4,2	7,8
TOC < 0,45 um (mg C/l)	6,6	5,8	5,0	4,4	3,8	4,1	7,6
TOC < 0,1 um (mg C/l)	7,0	6,5	5,6	4,8	4,2	3,8	4,4
Calculated removal results							
Col. < 11 um		36 %	77 %	85 %	-8 %	-7 %	-26 %
Col. < 1,2 um		58 %	77 %	87 %	90 %	90 %	43 %
Col. < 0,45 um		58 %	78 %	87 %	91 %	91 %	51 %
Col. < 0,1 um		57 %	77 %	87 %	92 %	94 %	90 %
UVA < 11 um		27 %	55 %	68 %	61 %	62 %	44 %
UVA < 1,2 um		35 %	54 %	67 %	75 %	76 %	50 %
UVA < 0,45 um		35 %	54 %	68 %	76 %	78 %	52 %
UVA < 0,1 um		33 %	51 %	66 %	75 %	80 %	81 %
TOC < 11 um		6 %	25 %	37 %	23 %	-7 %	-45 %
TOC < 1,2 um		15 %	26 %	39 %	42 %	42 %	-8 %
TOC < 0,45 um		11 %	24 %	34 %	42 %	38 %	-15 %
TOC < 0,1 um		8 %	20 %	32 %	41 %	45 %	37 %

Coagulant: Poly-Epi-amine (Cytec C-581)
pH : 6,0 +/- 0,1
Date: 25-sep-01

Dosage							
mg/l	0,00	1,0	2,5	5,0	7,5	14,8	19,9
mg/mg C	Raw-	0,2	0,5	0,9	1,4	2,7	3,6
ueq/mg C	water	1,3	3,2	6,3	9,5	18,8	25,2
Analysis results							
Turb. < 11 um (NTU)	0,34	1,37	0,94	0,23	4,84	3,25	0,43
Col. < 11 um (mg Pt/l)	48,6	54,5	31,3	11,3	31,8	75,3	51,9
Col. < 1,2 um (mg Pt/l)	47,7	50,7	17,7	8,9	5,1	39,3	44,3
Col. < 0,45 um (mg Pt/l)	45,3	42,4	16,5	8,3	4,6	37,6	43,6
Col. < 0,1 um (mg Pt/l)	43,8	27,3	16,0	8,0	4,0	10,7	31,3
UVA < 11 um (m^{-1})	26,3	27,8	18,3	11,0	9,9	20,9	24,3
UVA < 1,2 um (m^{-1})	26,5	27,3	16,4	11,1	7,9	19,5	22,5
UVA < 0,45 um (m^{-1})	26,2	24,9	16,2	10,7	7,5	19,1	21,7
UVA < 0,1 um (m^{-1})	25,4	20,7	16,2	10,9	8,1	7,8	16,3
TOC < 11 um (mg C/l)	5,5	6,2	5,2	4,0	3,8	9,5	12,7
TOC < 1,2 um (mg C/l)	5,4	6,0	4,9	4,0	3,4	8,3	11,5
TOC < 0,45 um (mg C/l)	5,7	6,2	5,1	4,3	3,8	8,7	11,7
TOC < 0,1 um (mg C/l)	6,1	5,7	5,3	4,5	4,2	4,9	9,8
Calculated removal results							
Col. < 11 um		-12 %	36 %	77 %	35 %	-55 %	-7 %
Col. < 1,2 um		-6 %	63 %	81 %	89 %	18 %	7 %
Col. < 0,45 um		6 %	64 %	82 %	90 %	17 %	4 %
Col. < 0,1 um		38 %	63 %	82 %	91 %	76 %	29 %
UVA < 11 um		-5 %	31 %	58 %	62 %	21 %	8 %
UVA < 1,2 um		-3 %	38 %	58 %	70 %	26 %	15 %
UVA < 0,45 um		5 %	38 %	59 %	71 %	27 %	17 %
UVA < 0,1 um		19 %	36 %	57 %	68 %	69 %	36 %
TOC < 11 um		-12 %	6 %	28 %	30 %	-72 %	-130 %
TOC < 1,2 um		-12 %	9 %	25 %	37 %	-54 %	-114 %
TOC < 0,45 um		-9 %	10 %	24 %	33 %	-53 %	-106 %
TOC < 0,1 um		6 %	13 %	27 %	31 %	20 %	-61 %

LMW CPAAM

Coagulant:	LMW CPAAM (Kemira Fennofix 240)
pH :	6,0 +/- 0,1
Date:	15-sep-01

Dosage							
mg/l	0,0	4,0	6,0	8,0	10,0	11,9	14,0
mg/mg C	Raw-	0,6	0,9	1,2	1,5	1,8	2,1
ueq/mg C	water	2,5	3,8	5,1	6,4	7,6	8,9
Analysis results							
Turb. < 11 um (NTU)	0,17	0,22	5,31	13,70	11,50	6,84	2,81
Col. < 11 um (mg Pt/l)	59,3	21,6	40,6	95,0	138,3	105,5	72,9
Col. < 1,2 um (mg Pt/l)	55,1	20,2	13,7	9,3	20,2	43,9	50,0
Col. < 0,45 um (mg Pt/l)	55,6	19,7	13,4	9,2	6,5	8,1	30,9
Col. < 0,1 um (mg Pt/l)	53,7	19,4	13,6	9,2	6,8	5,1	3,7
UVA < 11 um (m^{-1})	31,1	18,3	18,4	20,9	28,2	30,5	29,1
UVA < 1,2 um (m^{-1})	30,7	18,5	15,2	12,5	12,1	20,7	24,4
UVA < 0,45 um (m^{-1})	30,2	18,5	15,5	12,7	10,0	9,2	17,6
UVA < 0,1 um (m^{-1})	29,8	18,0	14,9	12,0	9,7	8,0	6,6
TOC < 11 um (mg C/l)	6,6	4,9	5,0	6,8	8,7	10,1	10,9
TOC < 1,2 um (mg C/l)	7,2	5,3	4,9	4,3	4,3	7,4	9,7
TOC < 0,45 um (mg C/l)	6,6	5,3	4,7	4,4	3,9	3,9	6,9
TOC < 0,1 um (mg C/l)	7,0	5,5	5,0	4,7	4,2	3,9	3,6
Calculated removal results							
Col. < 11 um		64 %	32 %	-60 %	-133 %	-78 %	-23 %
Col. < 1,2 um		63 %	75 %	83 %	63 %	20 %	9 %
Col. < 0,45 um		65 %	76 %	84 %	88 %	85 %	44 %
Col. < 0,1 um		64 %	75 %	83 %	87 %	91 %	93 %
UVA < 11 um		41 %	41 %	33 %	9 %	2 %	7 %
UVA < 1,2 um		40 %	50 %	59 %	61 %	33 %	21 %
UVA < 0,45 um		39 %	49 %	58 %	67 %	70 %	42 %
UVA < 0,1 um		40 %	50 %	60 %	68 %	73 %	78 %
TOC < 11 um		26 %	25 %	-3 %	-31 %	-53 %	-64 %
TOC < 1,2 um		27 %	33 %	40 %	41 %	-2 %	-35 %
TOC < 0,45 um		19 %	28 %	33 %	40 %	41 %	-5 %
TOC < 0,1 um		21 %	28 %	33 %	41 %	44 %	48 %

Coagulant: LMW CPAAM (Kemira Fennofix 240)
pH : 6,0 +/- 0,1
Date: 25-sep-01

Dosage							
mg/l	0,00	1,0	2,0	4,0	7,0	14,2	17,9
mg/mg C	Raw-	0,2	0,4	0,7	1,3	2,6	3,2
ueq/mg C	water	0,8	1,5	3,0	5,3	10,8	13,6
Analysis results							
Turb. < 11 um (NTU)	0,34	0,76	0,52	1,05	6,93	1,30	0,50
Col. < 11 um (mg Pt/l)	48,6	42,4	27,5	20,1	100,7	46,9	49,3
Col. < 1,2 um (mg Pt/l)	47,7	31,3	22,8	14,6	8,3	41,7	45,9
Col. < 0,45 um (mg Pt/l)	45,3	30,0	22,1	13,9	7,5	36,7	43,6
Col. < 0,1 um (mg Pt/l)	43,8	28,6	21,4	13,5	7,2	1,3	20,6
UVA < 11 um (m^{-1})	26,3	23,8	19,8	15,3	15,2	23,2	24,5
UVA < 1,2 um (m^{-1})	26,5	22,0	19,4	15,3	10,9	22,4	24,4
UVA < 0,45 um (m^{-1})	26,2	21,5	18,9	15,1	11,0	20,4	23,6
UVA < 0,1 um (m^{-1})	25,4	21,3	18,9	15,2	10,7	4,7	12,8
TOC < 11 um (mg C/l)	5,5	4,9	4,7	4,4	5,2	11,1	13,9
TOC < 1,2 um (mg C/l)	5,4	5,4	5,3	4,6	3,9	10,2	12,8
TOC < 0,45 um (mg C/l)	5,7	5,0	5,0	4,6	4,0	9,9	13,3
TOC < 0,1 um (mg C/l)	6,1	5,3	5,0	5,0	4,1	3,1	7,4
Calculated removal results							
Col. < 11 um		13 %	43 %	59 %	-107 %	4 %	-2 %
Col. < 1,2 um		34 %	52 %	69 %	83 %	12 %	4 %
Col. < 0,45 um		34 %	51 %	69 %	83 %	19 %	4 %
Col. < 0,1 um		35 %	51 %	69 %	84 %	97 %	53 %
UVA < 11 um		10 %	25 %	42 %	42 %	12 %	7 %
UVA < 1,2 um		17 %	27 %	42 %	59 %	16 %	8 %
UVA < 0,45 um		18 %	28 %	43 %	58 %	22 %	10 %
UVA < 0,1 um		16 %	26 %	40 %	58 %	81 %	50 %
TOC < 11 um		12 %	14 %	20 %	6 %	-100 %	-151 %
TOC < 1,2 um		-1 %	1 %	14 %	27 %	-90 %	-138 %
TOC < 0,45 um		12 %	12 %	19 %	29 %	-76 %	-135 %
TOC < 0,1 um		13 %	17 %	17 %	32 %	49 %	-21 %

MMW CPAAM

Coagulant: MMW CPAAM (Kemira Fennopol K1912)
pH : 6,0 +/- 0,1
Date: 15-sep-01

Dosage							
mg/l	0,0	4,0	6,0	8,0	10,0	12,0	14,0
mg/mg C	Raw-	0,6	0,9	1,2	1,5	1,8	2,1
ueq/mg C	water	2,4	3,6	4,8	6,0	7,2	8,4
Analysis results							
Turb. < 11 um (NTU)	0,17	1,20	4,38	5,57	5,05	6,47	6,70
Col. < 11 um (mg Pt/l)	59,3	32,9	45,2	78,7	69,5	68,9	58,7
Col. < 1,2 um (mg Pt/l)	55,1	22,0	15,6	11,5	9,1	6,7	5,6
Col. < 0,45 um (mg Pt/l)	55,6	21,5	15,0	11,1	8,8	7,2	5,5
Col. < 0,1 um (mg Pt/l)	53,7	21,4	15,8	11,6	9,1	6,7	5,6
UVA < 11 um (m^{-1})	31,1	21,0	19,2	19,1	16,7	15,0	13,6
UVA < 1,2 um (m^{-1})	30,7	19,2	16,5	13,8	11,7	9,7	8,5
UVA < 0,45 um (m^{-1})	30,2	19,3	16,4	13,8	11,9	10,1	8,7
UVA < 0,1 um (m^{-1})	29,8	18,6	16,1	13,6	11,7	9,6	8,6
TOC < 11 um (mg C/l)	6,6	5,2	5,1	5,0	5,0	5,0	5,2
TOC < 1,2 um (mg C/l)	7,2	5,3	5,1	4,7	4,5	4,0	4,0
TOC < 0,45 um (mg C/l)	6,6	5,5	5,1	4,9	4,5	4,3	4,0
TOC < 0,1 um (mg C/l)	7,0	5,8	5,5	5,2	5,2	4,8	4,4
Calculated removal results							
Col. < 11 um		45 %	24 %	-33 %	-17 %	-16 %	1 %
Col. < 1,2 um		60 %	72 %	79 %	84 %	88 %	90 %
Col. < 0,45 um		61 %	73 %	80 %	84 %	87 %	90 %
Col. < 0,1 um		60 %	71 %	78 %	83 %	87 %	90 %
UVA < 11 um		33 %	38 %	39 %	46 %	52 %	56 %
UVA < 1,2 um		37 %	46 %	55 %	62 %	68 %	72 %
UVA < 0,45 um		36 %	46 %	54 %	61 %	67 %	71 %
UVA < 0,1 um		38 %	46 %	54 %	61 %	68 %	71 %
TOC < 11 um		22 %	24 %	24 %	25 %	24 %	21 %
TOC < 1,2 um		27 %	29 %	35 %	37 %	45 %	45 %
TOC < 0,45 um		17 %	23 %	26 %	31 %	35 %	40 %
TOC < 0,1 um		17 %	21 %	26 %	25 %	31 %	38 %

Coagulant: MMW CPAAM (Kemira Fennopol K1912)
pH : 6,0 +/- 0,1
Date: 25-sep-01

Dosage					
mg/l	0,00	1,0	2,0	6,1	14,8
mg/mg C	Raw-	0,2	0,4	1,1	2,7
ueq/mg C	water	0,7	1,5	4,5	10,8
Analysis results					
Turb. < 11 um (NTU)	0,34	0,85	0,86	4,16	4,58
Col. < 11 um (mg Pt/l)	48,6	48,6	35,9	65,1	64,3
Col. < 1,2 um (mg Pt/l)	47,7	45,4	26,5	12,2	25,9
Col. < 0,45 um (mg Pt/l)	45,3	42,3	25,8	11,5	3,4
Col. < 0,1 um (mg Pt/l)	43,8	31,3	25,1	11,0	2,9
UVA < 11 um (m^{-1})	26,3	25,5	21,4	16,4	9,4
UVA < 1,2 um (m^{-1})	26,5	25,3	20,3	13,6	10,0
UVA < 0,45 um (m^{-1})	26,2	25,4	20,4	13,6	6,3
UVA < 0,1 um (m^{-1})	25,4	21,8	20,0	13,5	6,1
TOC < 11 um (mg C/l)	5,5	5,4	4,8	4,6	6,4
TOC < 1,2 um (mg C/l)	5,4	5,5	5,3	4,7	4,7
TOC < 0,45 um (mg C/l)	5,7	5,8	5,5	4,9	4,2
TOC < 0,1 um (mg C/l)	6,1	5,1	5,5	5,1	4,3
Calculated removal results					
Col. < 11 um		0 %	26 %	-34 %	-32 %
Col. < 1,2 um		5 %	45 %	74 %	46 %
Col. < 0,45 um		7 %	43 %	75 %	92 %
Col. < 0,1 um		29 %	43 %	75 %	93 %
UVA < 11 um		3 %	19 %	38 %	64 %
UVA < 1,2 um		5 %	24 %	49 %	62 %
UVA < 0,45 um		3 %	22 %	48 %	76 %
UVA < 0,1 um		14 %	21 %	47 %	76 %
TOC < 11 um		3 %	12 %	17 %	-16 %
TOC < 1,2 um		-3 %	1 %	12 %	13 %
TOC < 0,45 um		-2 %	2 %	13 %	27 %
TOC < 0,1 um		17 %	9 %	16 %	30 %

Coagulant: MMW CPAAM (Kemira Fennopol K1912)
pH : 6,0 +/- 0,1
Date: 26-nov-2001

Dosage							
mg/l	0,0	3,1	15,2	16,7	18,3	20,3	23,3
mg/mg C	Raw-	0,5	2,2	2,5	2,7	3,0	3,4
ueq/mg C	water	1,8	8,9	9,8	10,7	11,9	13,7
Analysis results							
Turb. < 11 um (NTU)	0,14	1,50	8,63	9,25	13,00	12,50	12,10
Col. < 11 um (mg Pt/l)	63,4						
Col. < 1,2 um (mg Pt/l)	62,3	32,6	6,7	6,3	4,9	6,8	32,0
Col. < 0,45 um (mg Pt/l)	60,2	30,6	6,2	5,4	4,5	3,3	8,0
Col. < 0,1 um (mg Pt/l)	58,2	29,6	6,3	5,2	4,1	3,2	2,6
UVA < 11 um (m^{-1})	33,1	25,9	15,3	13,8	12,4	14,0	24,1
UVA < 1,2 um (m^{-1})	34,4	24,6	10,3		8,2	7,8	16,3
UVA < 0,45 um (m^{-1})	35,0	24,8	23,9	7,5	8,6	7,5	6,5
UVA < 0,1 um (m^{-1})	33,1	24,3	10,8	9,8	8,7	7,4	6,7
TOC < 11 um (mg C/l)	6,8	6,3	6,6	6,2	12,5	8,5	11,2
TOC < 1,2 um (mg C/l)	6,9	5,9	4,6	4,4	3,2	4,0	7,4
TOC < 0,45 um (mg C/l)	7,4	6,7	4,7	4,4	4,2	3,8	4,4
TOC < 0,1 um (mg C/l)	7,1	6,6	4,7	4,6	4,8	4,5	4,4
Calculated removal results							
Col. < 11 um							
Col. < 1,2 um		48 %	89 %	90 %	92 %	89 %	49 %
Col. < 0,45 um		49 %	90 %	91 %	93 %	94 %	87 %
Col. < 0,1 um		49 %	89 %	91 %	93 %	95 %	96 %
UVA < 11 um		22 %	54 %	58 %	62 %	58 %	27 %
UVA < 1,2 um		28 %	70 %		76 %	77 %	52 %
UVA < 0,45 um		29 %	32 %	78 %	75 %	78 %	81 %
UVA < 0,1 um		27 %	67 %	70 %	74 %	78 %	80 %
TOC < 11 um		8 %	4 %	9 %	-84 %	-24 %	-64 %
TOC < 1,2 um		14 %	33 %	37 %	54 %	42 %	-6 %
TOC < 0,45 um		10 %	37 %	41 %	43 %	48 %	41 %
TOC < 0,1 um		6 %	34 %	35 %	33 %	36 %	38 %

Chitosan + iron chloride sulphate

Coagulant: Chitosan (F_A = 0,05) + iron chloride sulphate (Kemira JKL)

Date: 12-des-01

Dosage	Raw water				
Iron chloride sulphate (mg Fe/l)	0	1,0	1,0	2,0	2,0
Chitosan (mg/l)	0	1,0	2,0	1,0	2,0
Analysis results					
pH	6,0	5,9	5,8	5,8	5,8
Turb. < 11 um (NTU)	0,13	0,37	0,94	0,46	1,83
Col. < 11 um (mg Pt/l)	63,2	76,0	80,7	87,3	100,2
Col. < 1,2 um (mg Pt/l)	62,9	73,5	77,7	85,5	96,9
Col. < 0,45 um (mg Pt/l)	61,5	73,8	75,2	85,2	88,5
Col. < 0,1 um (mg Pt/l)	61,1	57,5	32,6	65,0	18,8
UVA < 11 um (m^{-1})	34,5				
UVA < 1,2 um (m^{-1})	34,2	38,2	38,9	43,0	43,9
UVA < 0,45 um (m^{-1})	34,3	38,3	38,5	43,2	42,0
UVA < 0,1 um (m^{-1})	34,2	33,5	25,0	36,0	17,8
TOC < 11 um (mg C/l)	7,4	7,9	8,5	7,5	8,7
TOC < 1,2 um (mg C/l)	7,2	7,8	8,3	7,8	8,5
TOC < 0,45 um (mg C/l)	7,0	7,0	7,1	7,4	7,9
TOC < 0,1 um (mg C/l)	7,6	7,3	6,0	6,6	5,1
Calculated removal results					
Col. < 11 um		-21 %	-28 %	-39 %	-59 %
Col. < 1,2 um		-17 %	-23 %	-36 %	-54 %
Col. < 0,45 um		-21 %	-23 %	-40 %	-45 %
Col. < 0,1 um		6 %	46 %	-7 %	69 %
UVA < 11 um					
UVA < 1,2 um		-11 %	-13 %	-25 %	-27 %
UVA < 0,45 um		-11 %	-12 %	-25 %	-22 %
UVA < 0,1 um		3 %	28 %	-4 %	48 %
TOC < 11 um		-6 %	-15 %	-1 %	-18 %
TOC < 1,2 um		-8 %	-15 %	-9 %	-18 %
TOC < 0,45 um		0 %	-2 %	-6 %	-13 %
TOC < 0,1 um		4 %	20 %	13 %	32 %

Coagulant: Chitosan ($F_A = 0,05$) + iron chloride sulphate (Kemira JKL)

Date: 12-des-01

Dosage	Raw water				
Iron chloride sulphate (mg Fe/l)	0	1,0	1,0	2,0	2,0
Chitosan (mg/l)	0	1,0	2,0	1,0	2,0
Analysis results					
pH	5,0	4,9	5,1	4,8	4,8
Turb. < 11 um (NTU)	0,13	0,7	0,4	1,3	0,2
Col. < 11 um (mg Pt/l)	57,4	75,0	42,6	90,1	23,6
Col. < 1,2 um (mg Pt/l)	56,3	70,1	30,8	81,6	20,0
Col. < 0,45 um (mg Pt/l)	56,8	69,4	29,0	81,3	19,5
Col. < 0,1 um (mg Pt/l)	56,8	39,6	29,1	29,0	19,3
UVA < 11 um (m^{-1})	33,9	37,6	27,8	43,3	18,8
UVA < 1,2 um (m^{-1})	33,8	36,7			
UVA < 0,45 um (m^{-1})	34,1	36,8	23,1	40,4	18,1
UVA < 0,1 um (m^{-1})	34,4	27,3	23,4	23,6	17,7
TOC < 11 um (mg C/l)	7,5	7,7	6,2	7,7	4,7
TOC < 1,2 um (mg C/l)	7,2	6,7	5,8	7,5	4,9
TOC < 0,45 um (mg C/l)	7,1	7,4	5,6	7,5	4,6
TOC < 0,1 um (mg C/l)	7,7	6,7	6,1	7,8	5,0
Calculated removal results					
Col. < 11 um		-31 %	26 %	-57 %	59 %
Col. < 1,2 um		-24 %	45 %	-45 %	64 %
Col. < 0,45 um		-22 %	49 %	-43 %	66 %
Col. < 0,1 um		30 %	49 %	49 %	66 %
UVA < 11 um		-11 %	18 %	-28 %	45 %
UVA < 1,2 um		-9 %			
UVA < 0,45 um		-8 %	32 %	-18 %	47 %
UVA < 0,1 um		21 %	32 %	31 %	49 %
TOC < 11 um		-4 %	16 %	-4 %	36 %
TOC < 1,2 um		7 %	19 %	-4 %	33 %
TOC < 0,45 um		-5 %	21 %	-7 %	34 %
TOC < 0,1 um		12 %	20 %	-3 %	35 %

Coagulant:	Chitosan ($F_A = 0,05$) + iron chloride sulphate (Kemira JKL)
Date:	12-des-01

Dosage	Raw water			
Iron chloride sulphate (mg Fe/l)	0	1,5	1,5	1,5
Chitosan (mg/l)	0	1,5	1,5	1,5
Analysis results				
pH	5,5	5,4	5,4	5,4
Turb. < 11 um (NTU)	0,12	0,96	0,77	0,66
Col. < 11 um (mg Pt/l)	60,3	85,6	83,9	82,9
Col. < 1,2 um (mg Pt/l)	61,0	81,3	80,0	79,1
Col. < 0,45 um (mg Pt/l)	58,8	81,5	80,2	79,2
Col. < 0,1 um (mg Pt/l)	58,6	34,6	38,3	39,5
UVA < 11 um (m^{-1})	34,2			
UVA < 1,2 um (m^{-1})	34,2	40,1	40,2	39,9
UVA < 0,45 um (m^{-1})	34,5	40,7	40,6	40,4
UVA < 0,1 um (m^{-1})	34,0	25,1	26,6	27,3
TOC < 11 um (mg C/l)	7,3	8,0	7,9	7,8
TOC < 1,2 um (mg C/l)	7,2	7,9	8,0	6,8
TOC < 0,45 um (mg C/l)	6,9	7,7	7,2	8,0
TOC < 0,1 um (mg C/l)	7,5	5,9	6,2	6,5
Calculated removal results				
Col. < 11 um		-42 %	-39 %	-37 %
Col. < 1,2 um		-33 %	-31 %	-30 %
Col. < 0,45 um		-39 %	-36 %	-35 %
Col. < 0,1 um		41 %	35 %	33 %
UVA < 11 um				
UVA < 1,2 um		-18 %	-18 %	-17 %
UVA < 0,45 um		-18 %	-18 %	-17 %
UVA < 0,1 um		26 %	22 %	20 %
TOC < 11 um		-9 %	-6 %	-6 %
TOC < 1,2 um		-9 %	-10 %	6 %
TOC < 0,45 um		-10 %	-3 %	-14 %
TOC < 0,1 um		22 %	18 %	14 %

PDADMAC + iron chloride sulphate

Coagulant:	PDADMAC (Cytec C-591) + iron chloride sulphate (Kemira JKL)
Date:	12-des-01

Dosage	Raw water				
Iron chloride sulphate (mg Fe/l)	0	1,0	1,0	2,0	2,0
PDADMAC (mg/l)	0	1,0	2,0	1,0	2,0
Analysis results					
pH	6,0	5,9	5,9	5,8	5,8
Turb. < 11 um (NTU)	0,13	0,50	1,96	0,88	1,30
Col. < 11 um (mg Pt/l)	63,2	78,9	93,5	91,8	93,4
Col. < 1,2 um (mg Pt/l)	62,9	76,8	87,1	89,2	89,3
Col. < 0,45 um (mg Pt/l)	61,5	76,6	62,5	88,9	87,7
Col. < 0,1 um (mg Pt/l)	61,1	55,3	24,7	55,1	24,7
UVA < 11 um (m^{-1})	34,5				
UVA < 1,2 um (m^{-1})	34,2	39,2	37,5	44,0	43,1
UVA < 0,45 um (m^{-1})	34,3	39,2	32,6	44,3	43,0
UVA < 0,1 um (m^{-1})	34,2	32,4	21,4	32,5	20,3
TOC < 11 um (mg C/l)	7,4	7,9	8,4	7,9	8,2
TOC < 1,2 um (mg C/l)	7,2	8,1	8,4	8,0	8,2
TOC < 0,45 um (mg C/l)	7,0	7,8	7,1	8,0	7,4
TOC < 0,1 um (mg C/l)	7,6	7,0	5,7	7,4	5,4
Calculated removal results					
Col. < 11 um		-25 %	-48 %	-46 %	-48 %
Col. < 1,2 um		-22 %	-38 %	-42 %	-42 %
Col. < 0,45 um		-26 %	-3 %	-46 %	-44 %
Col. < 0,1 um		9 %	60 %	10 %	60 %
UVA < 11 um					
UVA < 1,2 um		-14 %	-9 %	-28 %	-25 %
UVA < 0,45 um		-14 %	5 %	-28 %	-25 %
UVA < 0,1 um		6 %	38 %	6 %	41 %
TOC < 11 um		-7 %	-14 %	-7 %	-11 %
TOC < 1,2 um		-12 %	-17 %	-11 %	-13 %
TOC < 0,45 um		-12 %	-1 %	-14 %	-5 %
TOC < 0,1 um		7 %	24 %	2 %	29 %

Coagulant:	PDADMAC (Cytec C-591) + iron chloride sulphate (Kemira JKL)
Date:	12-des-01

Dosage	Raw water				
Iron chloride sulphate (mg Fe/l)	0	1,0	1,0	2,0	2,0
PDADMAC (mg/l)	0	1,0	2,0	1,0	2,0
Analysis results					
pH	5,0	4,8	4,8	4,8	4,9
Turb. < 11 um (NTU)	0,13	0,64	0,59	1,52	0,16
Col. < 11 um (mg Pt/l)	57,4	75,5	39,5	91,8	18,1
Col. < 1,2 um (mg Pt/l)	56,3	71,3	25,6	84,5	14,5
Col. < 0,45 um (mg Pt/l)	56,8	71,3	22,9	82,1	14,2
Col. < 0,1 um (mg Pt/l)	56,8	41,6	21,2	22,8	13,8
UVA < 11 um (m^{-1})	33,9	37,8	25,3	43,6	15,6
UVA < 1,2 um (m^{-1})	33,8	36,9			
UVA < 0,45 um (m^{-1})	34,1	37,2	20,4	40,6	15,0
UVA < 0,1 um (m^{-1})	34,4	28,0	19,8	19,1	14,9
TOC < 11 um (mg C/l)	7,5	7,4	6,5	8,1	4,5
TOC < 1,2 um (mg C/l)	7,2	8,0	5,6	7,8	4,5
TOC < 0,45 um (mg C/l)	7,1	7,8	5,5	7,6	4,2
TOC < 0,1 um (mg C/l)	7,7	6,9	5,9	5,4	4,6
Calculated removal results					
Col. < 11 um		-32 %	31 %	-60 %	68 %
Col. < 1,2 um		-27 %	55 %	-50 %	74 %
Col. < 0,45 um		-26 %	60 %	-45 %	75 %
Col. < 0,1 um		27 %	63 %	60 %	76 %
UVA < 11 um		-12 %	25 %	-29 %	54 %
UVA < 1,2 um		-9 %			
UVA < 0,45 um		-9 %	40 %	-19 %	56 %
UVA < 0,1 um		19 %	42 %	44 %	57 %
TOC < 11 um		0 %	13 %	-10 %	40 %
TOC < 1,2 um		-11 %	23 %	-8 %	38 %
TOC < 0,45 um		-11 %	22 %	-8 %	40 %
TOC < 0,1 um		9 %	23 %	29 %	39 %

Coagulant:	PDADMAC (Cytec C-591) + iron chloride sulphate (Kemira JKL)			
Date:	12-des-01			

Dosage	Raw water			
Iron chloride sulphate (mg Fe/l)	0	1,5	1,5	1,5
PDADMAC (mg/l)	0	1,5	1,5	1,5
Analysis results				
pH	5,5	5,5	5,4	5,3
Turb. < 11 um (NTU)	0,12	1,00	0,96	1,26
Col. < 11 um (mg Pt/l)	60,3	86,6	86,0	89,1
Col. < 1,2 um (mg Pt/l)	61,0	82,4	82,1	84,5
Col. < 0,45 um (mg Pt/l)	58,8	81,9	82,1	83,3
Col. < 0,1 um (mg Pt/l)	58,6	38,7	34,3	27,6
UVA < 11 um (m^{-1})	34,2			
UVA < 1,2 um (m^{-1})	34,2	40,7	40,6	41,3
UVA < 0,45 um (m^{-1})	34,5	41,0	40,9	41,1
UVA < 0,1 um (m^{-1})	34,0	26,6	24,7	22,4
TOC < 11 um (mg C/l)	7,3	8,1	8,4	8,1
TOC < 1,2 um (mg C/l)	7,2	8,3	8,3	8,4
TOC < 0,45 um (mg C/l)	6,9	8,2	8,1	8,3
TOC < 0,1 um (mg C/l)	7,5	7,7	6,0	5,7
Calculated removal results				
Col. < 11 um		-44 %	-43 %	-48 %
Col. < 1,2 um		-35 %	-35 %	-39 %
Col. < 0,45 um		-39 %	-40 %	-42 %
Col. < 0,1 um		34 %	42 %	53 %
UVA < 11 um				
UVA < 1,2 um		-19 %	-19 %	-21 %
UVA < 0,45 um		-19 %	-18 %	-19 %
UVA < 0,1 um		22 %	27 %	34 %
TOC < 11 um		-10 %	-14 %	-10 %
TOC < 1,2 um		-15 %	-15 %	-16 %
TOC < 0,45 um		-16 %	-15 %	-18 %
TOC < 0,1 um		-1 %	20 %	24 %

Iron chloride sulphate

Coagulant:	Iron chloride sulphate (Kemira JKL)		
Date:	30-aug-01	and	31-aug-01

Analysis results

Dose (mg Fe/l)	pH	Turb. < 11 um (NTU)	Col. < 11 um (mg Pt/l)	Col. < 0,1 um (mg Pt/l)	TOC < 0,1 um (mg C/l)
Raw water	6,1	0,23	50,2	49,9	6,4
3,0	4,2	1,32	26,1		
3,0	6,3	1,05	115		
5,0	4,4	0,47	5,3		
5,0	6,2	4,18	156	9,68	6,53
5,0	6,1	3,90	153		
7,0	4,1	0,20	3,9		
7,0	6,0	0,69	22,1		
7,0	5,8	0,33	8,7		
10,0	5,5	0,10	2,2		
10,0	5,0	0,10	1,2		

Relative removals

Dose	Col. < 11 um	Col. < 0,1 um	TOC < 0,1 um
3,0	48 %		
3,0	-130 %		
5,0	89 %		
5,0	-212 %	81 %	-2 %
5,0	-205 %		
7,0	92 %		
7,0	56 %		
7,0	83 %		
10,0	96 %		
10,0	98 %		

Coagulant: Iron chloride sulphate (Kemira JKL)
Date: 02-okt-01

Analysis results

Dose (mg Fe/l)	pH	Turb. < 11 um (NTU)	Col. < 11 um (mg Pt/l)	Col. < 0,1 um (mg Pt/l)	TOC < 0,1 um (mg C/l)
Raw water	6,0	0,19	60,4	60	7,4
3,0	4,3	2,61	50,5	6,9	3,1
3,0	5,0	3,58	123	10,4	
3,0	5,2	3,18	127	10,7	3,9
5,0	4,2	3,74	67,9	4,0	2,2
5,0	4,5	3,44	76,1		3,8
5,0	4,8	3,30	65,5	2,6	2,5
5,0	5,5	2,89	70,5	4,3	2,9
7,0	4,7	0,89	16,7	1,1	1,9
7,0	4,9	1,31	31,9		
7,0	5,7	1,47	28,8	2,2	2,5
7,0	6,3	1,73	49,9	4,4	2,8
10,0	4,2	1,09	18,2	1,2	1,7
10,0	4,6	0,28			
10,0	5,0	0,24	1,5	0,6	1,9
10,0	5,6	0,43	4,2	1,0	1,9
10,0	6,6	1,48	38,2		

Relative removals

Dose	Col. < 11 um	Col. < 0,1 um	TOC < 0,1 um
3,0	16 %	89 %	59 %
3,0	-105 %	83 %	
3,0	-112 %	82 %	48 %
5,0	-13 %	93 %	71 %
5,0	-27 %		50 %
5,0	-9 %	96 %	67 %
5,0	-17 %	93 %	61 %
7,0	72 %	98 %	75 %
7,0	47 %		
7,0	52 %	96 %	67 %
7,0	17 %	93 %	63 %
10,0	70 %	98 %	77 %
10,0	100 %		
10,0	98 %	99 %	74 %
10,0	93 %	98 %	75 %
10,0	36 %		

APPENDIX – F

Raw data from experiments on biofilm reactor effluent

Chitosan

Coagulant:	Chitosan F_A = 0,05
pH :	6,0 +/- 0,1
Date:	08-nov-01

Dosage						
mg/l	3,6	10,6	18,1	25,2	32,2	39,2
ueq/l	16	47	81	112	144	175
mg/mg C (< 0,1 um)	0,2	0,6	1,0	1,5	1,9	2,3
Analysis results						
Turb. < 11 um (NTU)	3,46	0,79	5,24	6,97	6,70	8,29
UVA < 0,1 um (m^{-1})	31,7	24,8	21,9	24,3	29,7	29,3
TOC < 0,1 um (mg C/l)	16,1	14,3	13,2	13,3	14,5	14,5
COD < 11 um (mg O/l)	51,1	38,6	41,8	48,2	53,2	60,9
COD < 1,2 um (mg O/l)	42,5	33,5	32,9	33,8	37,0	35,9
COD < 0,1 um (mg O/l)	39,7	36,1	32,6	35,1	39,1	36,3
11 um > COD > 1,2 um*	8,6	5,1	8,9	14,4	16,2	25,0
1,2 um > COD > 0,1 um*	2,8	-2,6	0,3	-1,3	-2,1	-0,4
Calculated removal results (relative)						
UVA < 0,1 um	13 %	31 %	40 %	33 %	18 %	19 %
TOC < 0,1 um	7 %	17 %	24 %	23 %	16 %	16 %
COD < 0,1 um	14 %	22 %	29 %	24 %	15 %	21 %
Calculated removal results (absolute)						
UVA < 0,1 um	4,6	11,4	14,3	11,9	6,6	7,0
TOC < 0,1 um	1,1	3,0	4,1	3,9	2,8	2,8
COD < 0,1 um	6,3	9,9	13,4	10,9	6,9	9,7

* Calculated

Coagulant: Chitosan $F_A = 0,05$
pH : 6,0 +/- 0,1
Date: 05-des-01

Dosage						
mg/l	2,0	6,0	13,8	17,9	21,9	30,1
ueq/l	8,9	27	61	80	98	134
mg/mg C (< 0,1 um)	0,1	0,3	0,6	0,8	1,0	1,4
Analysis results						
Turb. < 11 um (NTU)	5,59	3,17	0,53	0,67	3,05	4,31
UVA < 0,1 um (m^{-1})	34,0	31,7	28,2	27,1	26,3	25,9
TOC < 0,1 um (mg C/l)	21,7	18,6	17,5	17,6	17,0	16,3
COD < 11 um (mg O/l)	67,1	57,3	50,5	46,2	50,9	54,3
COD < 1,2 um (mg O/l)	51,4	47,7	45,3	44,8	43,0	41,1
COD < 0,1 um (mg O/l)	51,7	47,2	44,1	44,4	43,6	42,7
11 um > COD > 1,2 um*	15,7	9,6	5,2	1,4	7,9	13,2
1,2 um > COD > 0,1 um*	-0,3	0,5	1,2	0,4	-0,6	-1,6
Calculated removal results (relative)						
UVA < 0,1 um	10 %	15 %	25 %	28 %	30 %	31 %
TOC < 0,1 um	-1 %	13 %	18 %	18 %	21 %	24 %
COD < 0,1 um	6 %	14 %	20 %	19 %	20 %	22 %
Calculated removal results (absolute)						
UVA < 0,1 um	3,6	5,8	9,3	10,5	11,2	11,6
TOC < 0,1 um	-0,3	2,8	3,9	3,8	4,4	5,1
COD < 0,1 um	3,1	7,6	10,7	10,4	11,2	12,1
Analysis results (samples draw after sedimentation)						
Turb. (NTU)		14,7	3,6	6,8		
COD (mg O/l)		85,0	58,3	59,5		
SS (mg/l)		30,2	14,0	1,1		

* Calculated

PDADMAC

Coagulant: PDADMAC (Cytec C-591)
pH : 6,0 +/- 0,1
Date: 08-nov-01

Dosage						
mg/l	2,3	6,8	11,5	16,0	20,6	25,1
ueq/l	14	42	72	99	127	155
mg/mg C (< 0,1 um)	0,1	0,4	0,7	0,9	1,2	1,5
Analysis results						
Turb. < 11 um (NTU)	9,45	19,20	7,25	2,30	3,66	6,01
UVA < 0,1 um (m^{-1})	31,6	25,2	20,6	18,1	15,9	15,0
TOC < 0,1 um (mg C/l)	17,6	15,1	12,7	11,5	11,4	11,8
COD < 11 um (mg O/l)	55,3	51,7	42,0	37,6	62,7	46,0
COD < 1,2 um (mg O/l)	45,6	37,1	34,5	33,0	38,2	49,6
COD < 0,1 um (mg O/l)	43,8	37,6	33,6	32,3	30,5	31,7
11 um > COD > 1,2 um*	9,7	14,6	7,5	4,6	24,5	-3,6
1,2 um > COD > 0,1 um*	1,8	-0,5	0,9	0,7	7,7	17,9
Calculated removal results (relative)						
UVA < 0,1 um	13 %	31 %	43 %	50 %	56 %	59 %
TOC < 0,1 um	-2 %	12 %	26 %	33 %	34 %	31 %
COD < 0,1 um	5 %	18 %	27 %	30 %	34 %	31 %
Calculated removal results (absolute)						
UVA < 0,1 um	4,6	11,1	15,7	18,2	20,3	21,2
TOC < 0,1 um	-0,3	2,1	4,5	5,8	5,9	5,4
COD < 0,1 um	2,2	8,4	12,4	13,7	15,5	14,3

* Calculated

Coagulant: PDADMAC (Cytec C-591)
pH : 6,0 +/- 0,1
Date: 05-des-01

Dosage						
mg/l	2,0	6,0	13,8	17,9	22,0	30,2
ueq/l	12	37	86	111	136	187
mg/mg C (< 0,1 um)	0,1	0,3	0,6	0,8	1,0	1,4
Analysis results						
Turb. < 11 um (NTU)	6,63	11,40	3,50	1,99	5,37	3,82
UVA < 0,1 um (m^{-1})	33,0	28,5	24,4	23,4	22,5	18,9
TOC < 0,1 um (mg C/l)	19,5	18,3	17,4	17,4	17,4	14,9
COD < 11 um (mg O/l)	68,0	62,2	48,6	47,1	50,0	59,6
COD < 1,2 um (mg O/l)	51,9	47,2	43,3	44,3	43,9	50,9
COD < 0,1 um (mg O/l)	47,8	43,9	41,2	41,9	41,6	36,5
11 um > COD > 1,2 um*	16,1	15,0	5,3	2,8	6,1	8,7
1,2 um > COD > 0,1 um*	4,1	3,3	2,1	2,4	2,3	14,4
Calculated removal results (relative)						
UVA < 0,1 um	12 %	24 %	35 %	38 %	40 %	50 %
TOC < 0,1 um	9 %	14 %	19 %	19 %	19 %	30 %
COD < 0,1 um	13 %	20 %	25 %	24 %	24 %	33 %
Calculated removal results (absolute)						
UVA < 0,1 um	4,5	9,0	13,1	14,1	15,1	18,7
TOC < 0,1 um	1,9	3,1	4,0	4,0	4,0	6,5
COD < 0,1 um	7,0	10,9	13,6	12,9	13,2	18,3
Analysis results (samples draw after sedimentation)						
Turb. (NTU)			14,9	16,8	28,3	
COD (mg O/l)			52,9	56,9	59,9	
SS (mg/l)			15,7	14,9	29,5	

* Calculated

Poly-Epi-amine

Coagulant:	Poly-Epi-amine (Cytec C-581)
pH :	6,0 +/- 0,1
Date:	08-nov-01

Dosage						
mg/l	2,0	6,0	10,0	14,0	15,0	22,3
ueq/l	14	42	70	98	105	156
mg/mg C (< 0,1 um)	0,1	0,3	0,6	0,8	0,9	1,3
Analysis results						
Turb. < 11 um (NTU)	7,57	14,10	11,00	24,60	22,90	3,88
UVA < 0,1 um (m^{-1})	32,7	26,8	25,0	19,2	18,7	15,2
TOC < 0,1 um (mg C/l)	17,6	15,9	14,2	12,8	12,7	11,8
COD < 11 um (mg O/l)	57,6	53,7	45,8	48,1	44,7	39,6
COD < 1,2 um (mg O/l)	46,3	44,2	36,3	34,7	35,4	33,7
COD < 0,1 um (mg O/l)	45,6	40,1	38,8	32,0	33,7	31,6
11 um > COD > 1,2 um*	11,3	9,5	9,5	13,4	9,3	5,9
1,2 um > COD > 0,1 um*	0,7	4,1	-2,5	2,7	1,7	2,1
Calculated removal results (relative)						
UVA < 0,1 um	10 %	26 %	31 %	47 %	48 %	58 %
TOC < 0,1 um	-2 %	8 %	18 %	26 %	26 %	31 %
COD < 0,1 um	1 %	13 %	16 %	30 %	27 %	31 %
Calculated removal results (absolute)						
UVA < 0,1 um	3,5	9,4	11,3	17,1	17,5	21,0
TOC < 0,1 um	-0,3	1,4	3,1	4,4	4,6	5,4
COD < 0,1 um	0,4	5,9	7,2	14,0	12,3	14,4

* Calculated

Coagulant: Poly-Epi-amine (Cytec C-581)
pH : 6,0 +/- 0,1
Date: 05-des-01

Dosage						
mg/l	2,0	6,0	14,0	18,2	21,8	30,1
ueq/l	14	42	98	127	153	211
mg/mg C (< 0,1 um)	0,1	0,3	0,7	0,8	1,0	1,4
Analysis results						
Turb. < 11 um (NTU)	6,87	10,50	10,90	6,73	4,35	4,82
UVA < 0,1 um (m^{-1})	33,8	28,9	24,2	23,5	22,0	19,4
TOC < 0,1 um (mg C/l)	22,5	19,5	18,5	18,8	16,2	17,0
COD < 11 um (mg O/l)	71,8	67,9	54,5	53,5	48,4	52,6
COD < 1,2 um (mg O/l)	58,5	36,1	45,2	46,5	42,5	46,2
COD < 0,1 um (mg O/l)	51,2	45,0	42,8	43,0	42,6	40,6
11 um > COD > 1,2 um*	13,3	31,8	9,3	7,0	5,9	6,4
1,2 um > COD > 0,1 um*	7,3	-8,9	2,4	3,5	-0,1	5,6
Calculated removal results (relative)						
UVA < 0,1 um	10 %	23 %	36 %	37 %	41 %	48 %
TOC < 0,1 um	-5 %	9 %	14 %	12 %	24 %	21 %
COD < 0,1 um	7 %	18 %	22 %	22 %	22 %	26 %
Calculated removal results (absolute)						
UVA < 0,1 um	3,8	8,7	13,3	14,1	15,5	18,1
TOC < 0,1 um	-1,1	2,0	2,9	2,7	5,2	4,4
COD < 0,1 um	3,6	9,8	12,0	11,8	12,2	14,2
Analysis results (samples draw after sedimentation)						
Turb. (NTU)				21,8	17,6	19,9
COD (mg O/l)				73,7	60,7	60,2
SS (mg/l)				19,8	16,8	26,3

* Calculated

LMW CPAAM

Coagulant: LMW CPAAM (Kemira Fennofix 240)
pH : 6,0 +/- 0,1
Date: 08-nov-01

Dosage						
mg/l	3,3	10,0	16,7	23,5	30,2	36,5
ueq/l	14	42	70	99	127	153
mg/mg C (< 0,1 um)	0,2	0,6	1,0	1,4	1,8	2,1
Analysis results						
Turb. < 11 um (NTU)	12,40	14,40	3,10	4,51	5,26	5,12
UVA < 0,1 um (m^{-1})	31,8	25,2	20,3	18,1	15,3	15,3
TOC < 0,1 um (mg C/l)	16,4	15,0	13,2	11,9	11,5	12,5
COD < 11 um (mg O/l)	55,6	49,3	39,9	42,7	49,5	62,1
COD < 1,2 um (mg O/l)	44,4	37,2	34,1	35,9	46,2	55,3
COD < 0,1 um (mg O/l)	42,2	38,3	34,9	32,7	30,2	32,1
11 um > COD > 1,2 um*	11,2	12,1	5,8	6,8	3,3	6,8
1,2 um > COD > 0,1 um*	2,2	-1,1	-0,8	3,2	16,0	23,2
Calculated removal results (relative)						
UVA < 0,1 um	12 %	30 %	44 %	50 %	58 %	58 %
TOC < 0,1 um	5 %	13 %	23 %	31 %	33 %	27 %
COD < 0,1 um	8 %	17 %	24 %	29 %	34 %	30 %
Calculated removal results (absolute)						
UVA < 0,1 um	4,4	11,0	15,9	18,2	21,0	21,0
TOC < 0,1 um	0,9	2,3	4,1	5,4	5,7	4,7
COD < 0,1 um	3,8	7,7	11,1	13,3	15,8	13,9

* Calculated

Coagulant: LMW CPAAM (Kemira Fennofix 240)
pH : 6,0 +/- 0,1
Date: 05-des-01

Dosage						
mg/l	2,0	6,0	13,8	18,1	21,8	30,3
ueq/l	8,5	25	58	76	92	127
mg/mg C (< 0,1 um)	0,1	0,3	0,6	0,8	1,0	1,4
Analysis results						
Turb. < 11 um (NTU)	7,72	9,48	5,45	2,82	3,32	4,70
UVA < 0,1 um (m^{-1})	35,0	30,4	25,3	23,7	22,9	21,5
TOC < 0,1 um (mg C/l)	18,6	18,4	17,1	17,2	16,2	17,4
COD < 11 um (mg O/l)	65,5	55,8	53,6	47,2	48,3	52,9
COD < 1,2 um (mg O/l)	53,5	47,0	44,4	41,2	42,3	43,2
COD < 0,1 um (mg O/l)	46,6	42,3	43,7	41,4	42,8	41,8
11 um > COD > 1,2 um*	12,0	8,8	9,2	6,0	6,0	9,7
1,2 um > COD > 0,1 um*	6,9	4,7	0,7	-0,2	-0,5	1,4
Calculated removal results (relative)						
UVA < 0,1 um	7 %	19 %	33 %	37 %	39 %	43 %
TOC < 0,1 um	13 %	14 %	20 %	20 %	25 %	19 %
COD < 0,1 um	15 %	23 %	20 %	24 %	22 %	24 %
Calculated removal results (absolute)						
UVA < 0,1 um	2,6	7,2	12,3	13,8	14,6	16,1
TOC < 0,1 um	2,8	3,0	4,3	4,2	5,2	4,0
COD < 0,1 um	8,2	12,5	11,1	13,4	12,0	13,0
Analysis results (samples draw after sedimentation)						
Turb. (NTU)			17,2	16,2	19,9	
COD (mg O/l)			60,2	71,0	53,5	
SS (mg/l)			19,6	18,0	27,4	

* Calculated

MMW CPAAM

Coagulant: MMW CPAAM (Kemira Fennopol K1912)
pH : 6,0 +/- 0,1
Date: 08-nov-01

Dosage						
mg/l	2,0	3,5	10,5	17,5	25,8	30,9
ueq/l	7,8	14	42	70	103	124
mg/mg C (< 0,1 um)	0,1	0,2	0,6	1,0	1,5	1,8
Analysis results						
Turb. < 11 um (NTU)	7,31	9,72	13,20	4,27	7,53	8,64
UVA < 0,1 um (m^{-1})	33,8	32,2	24,8	20,3	16,4	16,6
TOC < 0,1 um (mg C/l)	18,4	16,8	14,0	13,3	12,1	12,3
COD < 11 um (mg O/l)	55,0	55,7	46,6	40,0	46,9	51,5
COD < 1,2 um (mg O/l)	47,6	44,9	36,4	32,3	32,5	29,1
COD < 0,1 um (mg O/l)	45,1	40,9	33,3	34,4	30,4	32,5
11 um > COD > 1,2 um*	7,4	10,8	10,2	7,7	14,4	22,4
1,2 um > COD > 0,1 um*	2,5	4,0	3,1	-2,1	2,1	-3,4
Calculated removal results (relative)						
UVA < 0,1 um	7 %	11 %	32 %	44 %	55 %	54 %
TOC < 0,1 um	-7 %	3 %	19 %	23 %	30 %	29 %
COD < 0,1 um	2 %	11 %	28 %	25 %	34 %	29 %
Calculated removal results (absolute)						
UVA < 0,1 um	2,4	4,0	11,4	15,9	19,8	19,6
TOC < 0,1 um	-1,1	0,5	3,3	3,9	5,2	5,0
COD < 0,1 um	0,9	5,1	12,7	11,6	15,6	13,5

* Calculated

Coagulant: MMW CPAAM (Kemira Fennopol K1912)
pH : 6,0 +/- 0,1
Date: 05-des-01

Dosage						
mg/l	2,0	6,0	13,9	17,9	21,1	29,7
ueq/l	8,0	24	56	72	84	119
mg/mg C (< 0,1 um)	0,1	0,3	0,6	0,8	1,0	1,4
Analysis results						
Turb. < 11 um (NTU)	6,25	9,31	5,81	2,27	3,40	4,48
UVA < 0,1 um (m^{-1})	34,6	32,0	26,3	24,3	22,7	21,3
TOC < 0,1 um (mg C/l)	20,7	18,3	17,8	17,1	17,5	17,1
COD < 11 um (mg O/l)	72,5	67,8	54,5	48,1	49,3	58,2
COD < 1,2 um (mg O/l)	55,5	48,1	43,4	43,6	40,9	42,0
COD < 0,1 um (mg O/l)	50,3	46,9	42,1	41,6	43,2	42,9
11 um > COD > 1,2 um*	17,0	19,7	11,1	4,5	8,4	16,2
1,2 um > COD > 0,1 um*	5,2	1,2	1,3	2,0	-2,3	-0,9
Calculated removal results (relative)						
UVA < 0,1 um	8 %	15 %	30 %	35 %	39 %	43 %
TOC < 0,1 um	3 %	15 %	17 %	20 %	18 %	20 %
COD < 0,1 um	8 %	14 %	23 %	24 %	21 %	22 %
Calculated removal results (absolute)						
UVA < 0,1 um	2,9	5,6	11,2	13,2	14,8	16,2
TOC < 0,1 um	0,7	3,2	3,6	4,3	3,9	4,3
COD < 0,1 um	4,5	7,9	12,7	13,2	11,6	11,9
Analysis results (samples draw after sedimentation)						
Turb. (NTU)				11,3	13,2	11,0
COD (mg O/l)				54,1	50,3	61,0
SS (mg/l)				11,6	27,8	37,0

* Calculated

PDADMAC + iron chloride sulphate

Coagulant: PDADMAC (Cytec C-591) + iron chloride sulphate (Kemira JKL)
Date: 21-nov-01

Dosage						
Iron chloride sulphate (mg Fe/l)	0	5,6	11,2	16,8	5,6	5,6
PDADMAC (mg/l)	2	2	2	2	2	2
Analysis results						
pH	8,2	8,0	7,8	7,7	7,2	5,5
Turb. < 11 um (NTU)	6,50	2,60	1,70	1,20	2,50	0,90
UVA < 0,1 um (m^{-1})	34,3	30,0	25,8	22,4	24,4	16,7
COD < 11 um (mg O/l)	58,8	46,5	40,7	39,4	43,4	34,9
COD < 0,1 um (mg O/l)	37,8	36,9	33,3	29,2	31,7	27,0
Calculated removal results						
UVA < 0,1 um	13 %	24 %	35 %	43 %	38 %	58 %
COD < 11 um	31 %	45 %	52 %	54 %	49 %	59 %
COD < 0,1 um	15 %	17 %	25 %	34 %	28 %	39 %
Analysis results (samples drawn after dissolved air flotation) *						
COD (mg O/l)	81,5	56,8	51,0	38,8		
COD < 0,1 um (mg O/l)	45,3	42,8	42,9	38,6		

* Data kindly provided by Esa Melin (Melin *et al*, 2002)

Results from dissolved air flotation experiments

Coagulant: MMW CPAAM (Kemira testset*) + Iron chloride sulphate (Kemira JKL)
Date: 23-jan-02 and 30-jan-02

Dosage						
Iron chloride sulphate (mg Fe/l)	11,2	11,2	11,2	0,0	0,0	0,0
MMW CPAAM (mg/l)	1	2	3	2	4	6
Analysis results**						
COD (mg O/l)	71	62	57	111	92	75
SS (mg/l)	21	14	13	40	30	19

* Table 4-2
** Reported results represent the average of all results obtained with Kemira testset

Coagulant: Chitosan ($F_A = 0,05$) + Iron chloride sulphate (Kemira JKL)
Date: 23-jan-02 and 30-jan-02

Dosage				
Iron chloride sulphate (mg Fe/l)	11,2	11,2	0,0	0,0
Chitosan (mg/l)	2	3	2	6
Analysis results				
COD (mg O/l)	60	56	121	116
SS (mg/l)	21	24	40	45