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Cationic polyelectrolytes as primary coagulants for municipal wastewater treatment

Thesis for the degree doktor ingeniør

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Polina Pilipenko

SUMMARY

Chemical treatment is an established technique for wastewater purification used alone or as a pre-treatment before biological treatment. In spite of many advantages associated with it, the excessive sludge production makes this technology undesirable. Since the sludge produced during chemical treatment to a great extend is a precipitated metal phosphate/hydroxide, a complete or partial substitution of metal salt by a cationic polyelectrolyte may reduce the sludge production.

This dissertation investigates the potential of synthetic organic polyelectrolytes for removal of the particulate and colloid matter from municipal wastewater. In the first two chapters of the thesis the state of the art and the theoretical background are discussed. Chapter 3 presents the hypotheses proposed based on first two chapters. Chapter 4 describes the experimental design and procedures as well as analytical methods utilised. Chapter 5 is devoted to presentation and discussion of experimental results. In Chapter 6 the relationships between polymer structure, wastewater quality and treatment performance were established and models were proposed for prediction of polyelectrolyte dose and effluent quality. Chapter 7 consists of analysis of hypotheses and recommendations for polyelectrolyte selection. Finally, Chapter 8 concludes the work of this thesis.

The results of this thesis show that synthetic organic polyelectrolytes are effective coagulants for wastewater treatment. Both low and high molecular weight cationic polyelectrolytes can be used as solo primary coagulants and combined with low dosage inorganic coagulant. The optimum dosage of the low molecular weight polyelectrolyte (PDADMAC and P-Epi-DMA) is affected by the concentration of the particles, colloids and soluble organic matter. The specific dosage is significantly reduced with increasing concentration of the particulate matter. The soluble organic matter has a negative effect on the treatment efficiency and increases the optimum dosage.

The residual polyelectrolyte concentration is a function of dosage for each polyelectrolyte tested. The molecular weight within one type of polyelectrolyte has little effect on the residual polyelectrolyte concentration. Very high molecular weight polyelectrolytes (PAM and PE) have lower residuals than the PDADMACs and P-Epi-DMA. The optimisation of the rapid mixing and flocculation procedures is crucial for minimising residual polymer concentration.

The process of wastewater coagulation-flocculation by the low molecular weight polyelectrolytes can be satisfactory described using a statistical multilinear regression model and mathematical regression model. The proposed models allow accurate prediction of the optimum dosage.

Addition of a low dosage of inorganic salt (i.e. Fe) significantly improves suspended particles and colloids removal by polymers. The combined coagulant removes the ortho-phosphates as well. Coagulation by such a dual coagulant is satisfactory described by the mathematical regression model. The treatment efficiency can be predicted with 90% accuracy.

The interaction between polyelectrolyte and dissolved organic matter lead to production of complexes, observed as colloidal particles. The size of the particle aggregates produced depends on the concentration ratio polyelectrolyte/dissolved organics organics.

CONTENTS

1. STATE OF THE ART

1.1. Introduction

There are few problems that are as common to all countries, regardless of economic system and level of development, as environmental degradation. Rapid deforestation, land degradation, air pollution, water shortages and water contamination are as common to Asia as they are to Europe and America. Even if the manifestations and dimensions of environmental degradation differ depending on history, geography and level of development, the underlying causes of it are fundamentally similar.

The water-related problems are, to a great extent, caused by the growing world population, which consumes more and more water and produce an increasing amount of sewage. In order to prevent or limit the disturbance of the ecological balance of the receiving water, the wastewater has to be treated before being released to the environment.

Today's question is not: "to treat or not to treat?" but what treatment strategy should be chosen. For many cities in the developing world as well as for many Norwegian communities along the coast, the choice of treatment scheme is a balance between environmental and economical issue.

From an environmental point of view the chemical treatment alone may be a sustainable solution, especially for small communities at coastal areas with release of treated water to the sea. On the other hand, from a technological point of view, chemical treatment is a logical first step and it can always be followed at a later stage by a more advanced treatment process.

Therefore, chemical treatment is an attractive solution, and its popularity has increased since the CEPT (Chemically Enhanced Primary Treatment) concept was introduced, particularly for upgrading primary treatment plants. According "Statistics Norway" in 2003 in Norway chemical treatment alone accounted for 36% of the total hydraulic treatment capacity of 5.57 million PE. In addition to this, around 28 % of the total capacity undergo chemical treatment in addition to biological treatment. (Berge *et al.,* 2005)

Since the major part of impurities in wastewater is associated with particles and can be removed by precipitation, substantial reduction in these impurities may be achieved with chemical treatment (Ødegaard, 1997, 1999).

In conventional chemical treatment inorganic chemicals, i.e. aluminium or iron salts, are utilised as major coagulants. An efficient particle and colloid removal as well as phosphorous removal can be achieved using metal-salt coagulants (Ødegaard, 1991).

However, a large amount of sludge results from the use of inorganic coagulants, that makes sludge handling a major cost factor for the chemical treatment process.

In the middle of last century, with the development of a chemical industry, the organic polymers were introduced to the treatment of wastewater. Since then, the synthetic organic polyelectrolytes have been primarily used as coagulant aids (non-ionic and anionic polymers). The cationic polyelectrolytes represent, however, an adequate substitute for traditional inorganic coagulant.

The use of polyelectrolytes as primary coagulants was reported to have a considerable number of advantages (Nozaic *et al.*, 2001). The most important of which are the greater stability and reliability of operation and the lack of extra solids in the form of metal hydroxide. There is a lower level of dissolved ions in the product water and no residual added metal ions. Besides, in utilising cationic polymers instead of inorganic coagulants, the performance is less dependent on pH and the alkalinity is maintained.

Several investigations have been carried out in order to evaluate the performance of cationic organic polyelectrolytes as primary coagulants. Nevertheless, the choice of the polyelectrolyte and polyelectrolyte application procedure is not optimised. Besides, the effluent quality is often unpredictable, especially in wastewater treatment. It seemed, therefore, worthwhile to investigate the coagulation/flocculation of the municipal wastewater with polyelectrolytes.

The major goal of this research is to find out how to use synthetic cationic polyelectrolytes as primary coagulants for municipal wastewater treatment in an optimum way. The study is aimed at evaluating general polyelectrolyte efficiency. The reduction of polymer dose and residuals, and improving the quality of the effluent are the most important objectives of the process optimisation.

Due to a variety of interactions among the factors controlling polymeric flocculation it is often difficult to predict the optimum dose of polyelectrolyte or estimate the treatment efficiency at a given dose. In order to be able to predict optimum dose and effluent quality as well as to make the choice of polyelectrolyte a more scientific process, a study of the coagulation mechanism was considered necessary. The study involves an investigation of the interactions between polyelectrolyte and wastewater impurities.

The determination of residual polyelectrolyte concentration was included in the study as a consequence of the concern about possible unfavourable effect of the residual polyelectrolyte on the aquatic organisms.

1.2. Wastewater impurities

The character of wastewater impurities is decisive for the selection of treatment scheme. The literature data indicate that in the sewage most of the impurities are associated with particles (Ødegaard, 1987). This section is devoted to the size characterisation of impurities in sewage.

From the standpoint of colloidal science, wastewater is a complex system containing polymorph and polydisperse colloids and particles in an electrolytic solution. Water impurities range in size from the true solutes, i.e. ions and molecules, to the suspended particles visible to the naked eye.

1.2.1. Characterization of wastewater impurities

The first attempt to classify the wastewater particulate matter was performed by Imhoff (1939). The whole spectrum of wastewater impurities was divided into three groups:

- settleable suspended matter;
- non-settleable suspended matter;
- soluble matter.

The study demonstrated that more than a half of the organic matter in the wastewater is associated with suspended solids.

In later works organic contaminants were divided into four groups:

- settleable;
- supracolloidal;
- colloidal;
- soluble.

Ødegaard (1987) have discussed and summarised (Table 1.1) the results of several American studies (Heukelekian and Balmat, 1959; Baltmat, 1957; Richert and Hunter, 1971).The studies demonstrated that only 25% of the COD is truly soluble (or smaller than 0.08μm) and about 40% of COD and TOC is non-settleable or associated with colloidal and supracolloidal particles.

The significance of these studies is that not only organics in wastewater were classified by size, but also biochemical oxidation rate was measured for each fraction. It is seen from the data in Table 1.1 that with increasing particle size oxidation rate decreases significantly. Ødegaard emphasises that this finding is an important argument for the particle separation prior to biological treatment (Ødegaard, 1987).

Table 1.1. Size classification of organic matter in wastewater (Heukelekian andBalmat, 1959; Baltmat, 1957; Richert and Hunter, 1971).

	Classification			
	Soluble <0.08 µm	Colloidal 0.08-1.0 µm	Supracolloidal 1-100 µm	Settleable > 100µm
Org. constit. (%)				
Grease	16	62	30	28
Protein	5	30	56	37
Carbohydrates	79	8	14	35
Biochemical oxid. rate, k, d^{-1}	0.39	0.22	0.09	0.08

Spérandio *et al.*(Spérandio *et al.*,2000) and Anderson *et al.(*Anderson *et al.,* 2001) performed research on the fractionation of COD in France. A similar investigation was performed in the Netherlands (STOWA, 1999) and earlier in Norway (Østerhus, 1991). The results of these investigations are summarised in Table 1.2. In spite the variations observed it is clear that 60% or more of COD is associated with colloidal and larger particles. In Norwegian study Melin *et al.*(2002) distinguished four COD fractions. The results of this study are presented in Fig. 1.1.

Table 1.2. COD related to particles and dissolved COD in wastewaters.

Country	**COD**	**COD soluble**		**COD particulate**	
	mg/l	mg/l	%	mg/l	%
France* (Spérandio *et al.*,2000)	633±169	260±106	40	373±125	60
Netherlands* (Anderson *et al.,* 2001; STOWA, 1999)	557±146	140±44	25	417±142	75
Norway** (Østerhus, 1991)	278±104	101±40	36	-	64

* particles < 0,45 µm were classified as dissolved COD
** particles < 1 µm were classified as dissolved COD

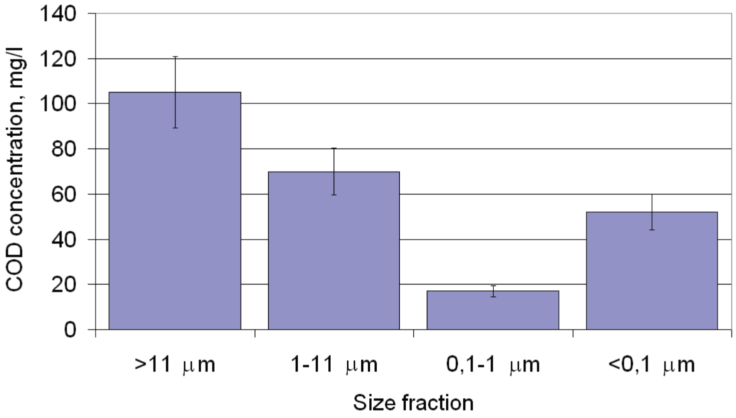


Fig. 1.1. The average COD concentration in different particle size fractions of municipal wastewater. (Melin et al., 2002)

Due to eutrophication problems, the requirements for removal of nutritients from wastewater have increased. Studies involving the investigation of total phosphorus and organic nitrogen were performed by Munch *et al.* (1980), Ødegaard (1999). The results (Table 1.3) demonstrated that most of the phosphorous in wastewater appear as soluble phosphates, but nevertheless, the amount of phosphorous associated with particles was 37%. The amount of organic nitrogen associated with particles was more significant and 73% of total organic nitrogen was found in colloidal or particular form.

Table 1.3. Classification of contaminants in wastewater (Munch et al., 1980).

	Classification			
	Soluble <0.025µm	Colloidal 0.025-3 µm	Supracolloidal 3-106µm	Settleable >106 µm
BOD_5 (% of total)	17	16	46	21
COD (% of total)	12	15	30	43
TOC (% of total)	22	6	36	36
Tot. P (% of total)	63	3	12	22
Org. N (% of total)	27	15	38	20

In the Dutch research the wastewater from the eight wastewater treatment plants in the Netherlands was fractionated and an “average” wastewater composition was determined (Nieuwenhuijzen, 2002). The results are presented in Table 1.4. The study illustrates that the fraction of COD related to settleable particles is 21%. A major part of COD

(38%), BOD (44%) and phosphorous (35%) is present in suspended and supra-colloidal particle fractions.

Table 1.4. Average wastewater composition in Netherlands (Nieuwenhuijzen, 2002)

Parameter	**Fraction**						Raw influent mg/l
	Dissolved <0.1μm	supra dissolved 0.1-0.45μm	colloidal 0.45-1.2μm	supra colloidal 1.2-5μm	suspended 5-63mm	settleable >63μm	
TSS, %	-	-	-	-	52(±18)	48(±18)	130
Turbidity, %	-	-	7(±4)	10(±7)	62(±17)	21(±12)	116
BOD_5, %	48(±12)	-	-	14(±6)	30(±8)	8(±4)	170
COD, %	36(±10)	3(±4)	2(±2)	11(±6)	27(±11)	21(±9)	461
N_{total}, %	83(±25)	1(±1)	3(±3)	4(±2)	5(±3)	4(±4)	43.7
P_{total}, %	53(±18)	3(±3)	3(±1)	5(±2)	30(±12)	6(±3)	7.7

Fig. 1.2 categorises the more significant water dispersed organic species by size (Levine *et al.*, 1985). As is seen from the data, bacteria and viruses are particles in the size range of about 0.01-10μm, and even if some of the viruses are very small (0.01-0.1μm), several investigations (Lewis *et al.*, 1986; Wellings *et al.* 1976; Vasl and Kott, 1982) have demonstrated that 60-100% of the viruses in sewage are adsorbed on particles.

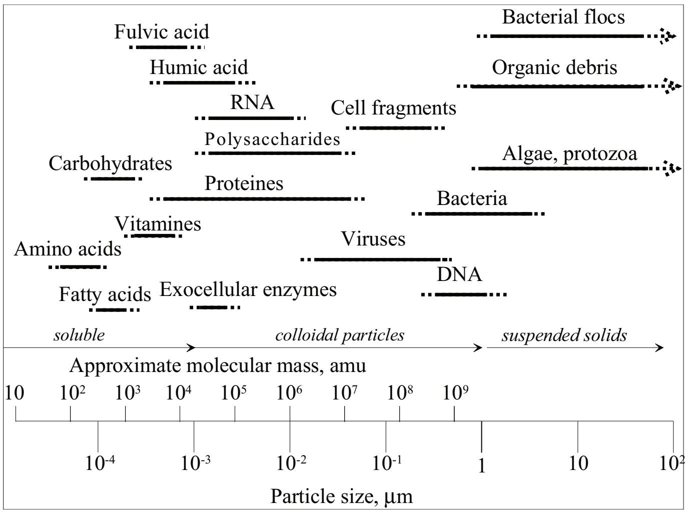


Fig. 1.2. Typical organic constituents in settled municipal wastewater. (Levine et al., 1985).

Also other contaminants such as metals and organic micro-pollutants are strongly associated with particles. A Swedish study have demonstrated that the percentage of total metal content associated to suspended matter in the raw wastewater was in the range of 50-75% for Zn, Cu, Cr, Pb, Cd and only 13% for nickel (Ødgaard,1999). The organic micropollutans as PCB and PAH were found to have high affinity to particulate matter (Luin and Starkenburg, 1984; Ødegaard 1999).

Thus, as was demonstrated by many researchers, a very significant part of contaminants in wastewater is associated with particles. Consequently a significant contaminant reduction may be expected as a result of particle elimination.

Several researchers particularly emphasised that the size of suspended solids has considerable impact on separation processes such as sedimentation, flocculation and filtration (Alon and Adin, 1994; Kavanaugh *et al.*, 1980; Tiehm *et al.*, 1999; Stevenson, 1997, Inoue et al., 2004).

The efficiency of such process as coagulation – flocculation can be affected by particle size distribution. Adin (1999) demonstrated that the removal efficiency of colloidal and larger particles varies considerably, particularly in ferric chloride coagulation.

The efficiency of coagulation flocculation can be studied by comparing the particle size distribution before and after the addition of coagulant. A variety of techniques is available for the characterisation of particle size distribution; however the standardised analytical technique does not currently exist. Among the techniques to measure particle size are: microscopic analysis, light scattering and membrane filtration (Lawler, 1997, Neis and Tiehm, 1997, Aguilar *et al*., 2003, Melin *et al* 2002).

1.3. Physical-chemical treatment and chemically enhanced primary treatment

In general a wastewater treatment train may include preliminary, primary, secondary and advanced treatment. The preliminary and primary treatments are based on physical processes, while secondary treatment is based on biological and/or chemical processes.

The Norwegian treatment philosophy is based on the fact that a significant improvement in sewage quality can be achieved by particle elimination. The experience with chemical treatment in Norway shows that on average 90% of SS and 73% of COD is removed. Since, treatment plants use inorganic coagulants, 94% of phosphorous is removed as well (Ødegaard, 1992).

There are two types of chemical treatment plants built in Norway: primary precipitation plants and secondary precipitation plants (Fig. 1.3). The primary precipitation plant does not include a primary sedimentation stage. The results from 87 Norwegian chemical treatment plants indicate that there is no significant difference in performance of primary and secondary precipitation plants (Ødegaard, 1992).

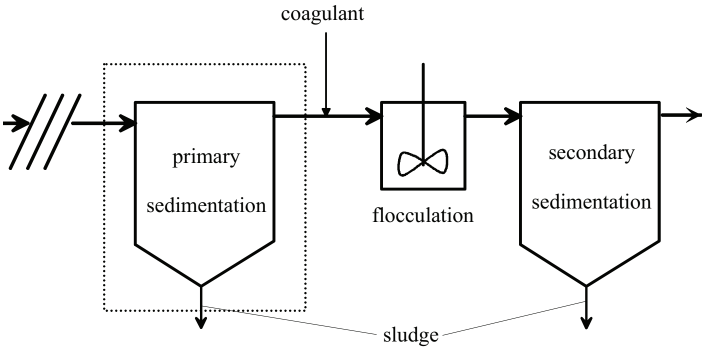


Fig. 1.3. Schematic representation of chemical treatment plant.

The concept of chemically enhanced primary treatment (CEPT), which is actually an "old" primary treatment plant upgraded by addition of coagulant, is becoming more and more popular. In CEPT, raw sewage is pumped into primary sedimentation tanks where the addition of chemicals is carried out to enhance sedimentation (D'Souza, 1995). The CEPT is preferred to primary treatment alone because it can remove twice as much pollution as primary treatment and it can also reduce the size and cost of the subsequent secondary treatment (Environmental Protection Department, 1995).

The CEPT has a potential as an enhancement of primary treatment step in order to reduce load on the following biological step (Parker *et al.*, 2000; Narayanan *et al.*, 2000), and as a cost-effective solo treatment for the mega-cities of developing world (Harleman and Murcott, 1999).

No matter what name is given to the chemical treatment, the idea is unchanged: special chemicals, called coagulants, are added to wastewater to induce particle aggregation.

The salts of polyvalent metals are traditionally used as coagulants. In Norway (1992) 83% of chemical treatment plants use aluminium salts, 15% - use iron salts and 2% - use lime as a coagulant. These treatment plants produce 0,65 kg dry solids per m^3 of water treated.(Berge *et al.,* 2005). Before 2003 around 46% of sludge had to be deposited on the special waste fields (Ødegaard, 1992). From 2003 Norwegian authorities imposed a ban on such deposition. Therefore, the reduction of sludge production has become an important issue.

The sludge produced during chemical treatment is comprised of solids removed from the wastewater and precipitated metal hydroxide. Therefore, one way to reduce sludge production is a partial or total substitution of metal coagulant by organic polyelectrolyte.

1.4. Experience with polyelectrolytes

More than a half-century ago, synthetic organic polymers were introduced into environmental engineering. Since then they have been used in water and wastewater treatment processes. For many years the main purpose of synthetic organic polymers was to aid in coagulation. The polymers were applied after inorganic coagulants to improve strength and settleability of floc, produced by an inorganic coagulant. However, the use of polymers as primary coagulants is increasing.

1.4.1. The use of polymers in drinking water treatment

In water treatment, synthetic organic polymers are used as primary coagulants as well as in the more traditional flocculation step of binding already formed small flocs into larger aggregates. Cationic polyelectrolytes are effective for both turbidity and natural organic matter removal (Veitser and Sterina, 1969; Amy and Chadik, 1983, Narkis and Rebhun, 1983, Bolto *et al.*, 1998, Nozaic, 2001)

Polyelectrolytes are nearly as efficient for humus removal as alum, taking out 86 to 100% of the colour that alum does (Bolto *et al.*, 1998). The efficiency of cationic polyacrylamide was found to be strongly MW dependent: polyacrylamide with a molecular weight of 10 million Dalton performed twice as well as polyacrylamide with a molecular weight of 2 million Dalton (Bolto *et al.*, 1998).

The other studies have found no effect of the molecular weight of the cationic polyelectrolytes (over a range from about 50000 to 15 million) on the humic substances removal (Kam and Gregory, 2001, Kvinnesland, 2002, Kvinnesland and Ødegaard, 2004). Leu and Ghosh, (1988) have demonstrated that the charge density rather than molecular weight is important in selecting the polyelectrolyte. Kvinnesland (2002) came to the same conclusion.

Kam and Gregory (2001) found that the optimum flocculation of humics occurred with less cationic charge in the case of low-charge polyelectrolytes than those with higher charge density. However, the degree of removal was considerably better in the latter case. Kvinnesland (2002) have shown that the extent of coagulation of humic substances, could, regardless of the polymer type, be explained by the amount of cationic charge equivalents added per mg TOC of humic substances.

In the presence of suspended solids low molecular mass polymers preferentially reacted with soluble organics, while high molecular mass polymers at low dosage preferentially reacted with suspended solids (Narkis and Rebhun, 1983). At a higher dosage, when the coverage of suspended solids surface by polymer increases, polymers begin to interact with humic substances. The presence of suspended solids brings about an increase in the degree of humic substance removal (Narkis and Rebhun, 1983; Bolto *et al.*, 1999).

1.4.2. The use in wastewater treatment

In wastewater treatment the main applications of polymers are coagulation/ sedimentation and sludge conditioning. Cationic polyelectrolytes are not widely used as primary coagulants for wastewater, even though they have significant advantages over inorganic coagulants. The process is more stable; polymers perform efficiently in a wide range of pH, the polymer dosage is practically independent on alkalinity and ionic strength of the media, polymers do not affect the pH of treated water (Fettig *et al.*,1990, Nozaic *et al.*, 2001, Mels, 2002). Significant reduction of a sludge volume, when a polyelectrolyte was used as a primary coagulant was observed. (Veitser and Mints, 1984, Nozaic *et al.*, 2001). Sludge produced by the High molecular weight polyelectrolytes were reported to produce large well settling flocs (Nieuwenhuijzen, 2002, Mels, 2002).

The main disadvantage of cationic polyelectrolytes as primary coagulants is their inability to remove phosphates from wastewater. But, when elimination of phosphates is necessary, a combined use of inorganic coagulant and cationic polyelectrolyte can be utilized, as reported by Sørensen (1992). Besides, a combined use of iron salt and cationic polyelectrolyte makes the reduction of the amount of iron salt needed for coagulation possible. Melin *et al.* (2002) reported that good SS removal can be obtained by dissolved air flotation when low dosages of iron and polymer are combined. Moreover, sludge produced in the combined process is more readily biodegradable because of lower inorganic content (Sørensen, 1992).

Zhou *et al.* (1995) reported that polyethyleneimine, if used as the primary coagulant, can remove 80% of phosphate from wastewater. In this study a membrane filtration technique called “liquid-phase polymer-based retention” was utilised.

The performance of the polymer was found to be strongly dependent on wastewater characteristics. For instance, McLachlan *et al.* (1980) found that nonionic and slightly cationic polymers were effective coagulants for colloidal material removal from a highly concentrated industrial wastewater. While for municipal wastewater, only strongly cationic polymers were efficient for the removal of suspended solids. Slightly cationic polymers were less efficient (Fettig *et al.* 1990) Nieuwenhuijzen (2002) and Mels (2002) obtained good suspended solids removal with high molecular weight PAMs. Melin *et al.*(2002) observed no significant difference in performance between s and medium molecular weight PAMs.

Zemaitaitiene *et al.*(1998) investigated the complex formation of the polyquaternary ammonium salt. The results showed that polyquaternary salt was prone to form complexes with anionic detergent, dispersing agents, thickeners, and some inorganic colloidal compounds. The performance of polymer complexes for destabilisation of direct dye colloids improved, when compare to the performance of the pure polymer.

1.5. Fate of the polyelectrolyte

The fate of polyelectrolytes and their contaminants in treatment facilities and in the environment is a serious concern regarding the use of polyelectrolytes. The following questions arise:

1. Is all the added polyelectrolyte excluded from the system as sludge?
2. How does a residual polymer and its contaminants, such as monomers and additives, behave in the treatment stages following coagulation, and what by- products form during treatment.
3. How does the water containing residual polyelectrolyte influences on the aquatic live in receiving water?

Mallevialle *et al.* (1984) determined the ultimate fate of the anionic polyacrylamide and its by-products in the treatment train included clarification, rapid sand filtration, activated carbon adsorption, ozonation, and postchlorination. In addition to analysing for specific compounds, the mutagenicity of the polymer, its contaminants, and by-products was evaluated by the Ames test. The experimental results indicate that the ozonation transforms polymer and monomers into other forms of organic carbon, by-products of the oxidation appear to be innocuous, except those from acrylic acid. The by-products of ozonation of acrylic acid appear to be more mutagenic than the reactant. Besides, acrylic acid and acrylamide were found to be precursors to some chlorinated compounds. However, mutagenicity studies did not show significant effects from the chlorinated by-products. Adsorption tests show that polymers and monomers are weakly adsorbed into GAC, so the concentration that passes the sedimentation and filtration process will not be reduced on GAC.

In a laboratory simulation of a water treatment plant conducted by Croll *et al.* (1974) it was observed that 95% of the acrylamide in a polyacrylamide product added during the rapid mixing step was present in the settled water and 93% was present in the filtered water.

A number of studies have been carried out on the aquatic toxicity of polyelectrolytes (Biesinger, 1976; Biesinger and Stokes, 1986; Cary *et al.*, 1987; Timofeeva, 1994). The non-ionic and anionic polymers were found to be not acutely toxic to fish, while cationic polymers were very toxic and their toxicity varied widely with the chemical structure of polyelectrolyte (Biesinger, 1976; Biesinger and Stokes, 1986). The sensitivity to cationic polymers varies from species to species. For instance, cladoceran (*Daphnia magna*) was ten times as sensitive to the presence of cationic polyelectrolyte as rainbow trout (*Salmo gairdneri*). The tested animals died from suffocation caused by the formation of polymeric film on gills.

Timofeeva (Timofeeva, 1994) quantified the toxicity of cationic polyacrylamides towards daphnia and minnows as a function of molecular weight and charge density. The results indicate that the toxicity is greatest for the polymers of highest charge density, almost irrespective of chain length. Similar work was carried out with anionic polyacrylamides and daphnia. The most toxic were polymers of longer chain length, but they are at least a 100 times less toxic than the cationic versions.

As far as the polyamines (P-Epi-DMA) and PDADMACs are concern very little published information is available on their toxicity. Some of toxicological information on poly quaternary ammonium salts is presented in Table 1.5. The data indicate that is less toxic to fish and invertebrates than P-Epi-DMA. The study of Waller *et al.* (1993) has even shown that PDADMAC is less toxic to Rainbow Trout than chitosan.

The biodegradability and bioaccumulation data on and poly-Epi-DMA does not appear to be available at the moment. However studies undertaken with regard to DADMAC based surfactants indicate that a short-chained DADMAC was ultimately biodegradable in aerobic conditions (Larson, 1983, Larson and Vashon, 1983, Ginkel, 1995).

Cary *et al.* (Cary *et al.*, 1987) have shown that once adsorbed to colloidal matter or interacted with dissolved organics the polyelectrolyte is not acutely toxic to aquatic organisms. By adding a variety of suspended solids (such as bentonite, kaolin and silica) and dissolved organic substances (humic, fulvic and tannic acids) the toxicity of polyelectrolytes for the waterflea and the fathead minnow was decreased by between 10 and 100 times. The presence of dissolved organic matter reduces the toxicity more than the presence of suspended solids.

There is, also, a concern that the accumulation of organic polymers in lakes and rivers may increase precipitation of heavy metals in natural waters and therefore lead to the accumulation of these toxic materials in sediments (Hahn and Antusch, 1998).

Two studies focusing on management of polyelectrolytes in aquatic system (Murgatroyd e*t al*, 1996 and Lamberton, 1995) came to rather controversial conclusions. While Lamberton (1995) underlined that in any case where treated water has to be discharged into aqueous environment a beforehand risk assessment has to be carried out, Murgatroyd *et al.* concluded that in natural waters, due to adsorption of polyelectrolyte to a naturally occurring colloidal matter, any risk to aquatic life would be eliminated.

Dentel *et al.* (2000) claimed, based on the data from NMR and GPC that at optimal dosages for conditioning, most of the polymers will remain with solids. On the other hand, Becker *et al.* (2000), utilising a colloid titration technique, observed very high concentrations of residual polymers, especially when lower molecular weight polyelectrolytes were used.

Table 1.5. Effects of quaternary ammonium polyelectrolytes on aquatic species.

Species	**Polymer**	**LC50 (mg/l)**	**Duration**	**Reference**
Rainbow Trout	PDADMAC	0,64	48 h	Waller *et al.* (1993)
Channel Catfish	PDADMAC	1,90	48 h	Waller *et al.* (1993)
Rainbow Trout	PDADMAC	0,47	96 h	Accepta 2058. Material safety data sheet (2002)
Bluegill Sunfish	PDADMAC	0,90	96 h	Accepta 2058. Material safety data sheet (2002)
Fathead Minnow	PDADMAC	0,90	96 h	Accepta 2058. Material safety data sheet (2002)
Water Flea	PDADMAC	97	96 h	Accepta 2058. Material safety data sheet (2002)
Rainbow Trout	Poly-Epi-DMA	0,097	96 h	Accepta 2059. Material safety data sheet (2002)
Fathead Minnow	Poly-Epi-DMA	0,38	96 h	Accepta 2059. Material safety data sheet (2002)
Water Flea	Poly-Epi-DMA	0,7	96 h	Accepta 2059. Material safety data sheet (2002)

In spite of well-documented negative effect of cationic polyelectrolytes on different forms of aquatic life, as well as other possible environmental effects, the number of studies focussing on documentation of residual polyelectrolyte in the effluent is quite limited. One of the reasons is the lack of adequate technique for residual polyelectrolyte determination.

However, there are a number of methods available for determination of residual cationic polyelectrolytes in water, unfortunately, all of them have disadvantages. The most simple is the method based on the colloid titration principle, the method is described in details elsewhere (Burcket, 1970, Walter, 1978, Becker *et al.*, 2000). The method is unselective, has low detection limit and a large sample volume (50-100 ml) is necessary. High precision, selective methods are based on advanced techniques such as NMR and GPC and require, therefore, costly instrumentation and highly qualified personnel to perform analyses, which is not always available for wastewater treatment facilities. Since the method has to be accessible, easy to use, quick and precise, the spectrophotometric method, first described by Furlong and Elliker (1953), seems to be the most suitable one. This method is based on formation of coloured complexes between the quaternary ammonium group of a polyelectrolyte and eosin, followed by spectrophotometric quantification of the polyelectrolyte-eosin complex.

1.6. Summary

In this chapter the analysis of wastewater contamination with respect to particle size is given. The concept of physical-chemical as well as CEPT is stated and the experience with use of polyelectrolyte in water and wastewater treatment is reviewed. The fate of polyelectrolyte and an environmental impact of polyelectrolyte discharge are discussed.

The following conclusions can be drawn:

- The main contaminants in municipal wastewater are associated with particles. Although the variations can be observed, about 20% -35% of COD of wastewater is caused by soluble contaminants. A significant amount of phosphorous (30-50%) and nitrogen (20-35%) is also associated with colloids or larger particles. Effective particle removal on the early stage of the treatment train reduces the load on the following biological stage and improves the total treatment efficiency.
- Particle size distribution is important for the treatability of wastewater. There is a clear indication that with reducing particle size, higher doses of coagulant are necessary for effective particle removal. Chemical enhancement of primary sedimentation improves significantly process performance and allows removals up to 70% of COD.
- The use of inorganic salts as coagulants for wastewater is associated with some disadvantages, the main of which is large amount of sludge produced.

- In potable water treatment polyelectrolytes have been effectively used as primary coagulants for turbidity and natural organic matter removal.
- The use of polyelectrolytes as primary coagulants in municipal wastewater provides the possibility for a reduction of sludge production, improvement of sludge dewaterability and maintenance of pH and alkalinity under coagulation.
- The residual polyelectrolyte concentration in treated water needs to be better documented.

2. THEORETICAL BACKGROUND

2.1. Colloidal stability of wastewater particles

The colloidal system is called stable if its dispersity and concentration do not change with time. It has been found that the stability of hydrophilic colloids (colloids having a strong tendency to bind or absorb water) is much greater than the hydrophobic ones (water repellent colloids). The dispersion of hydrophilic colloids leads to a uniform distribution of the dispersed phase in the system, therefore the entropy (ΔS) increases and the free energy (ΔG) reduces.

$$\Delta G = \Delta H - T\Delta S < 0$$

Therefore, the hydrophilic colloids are thermodynamically stable.
The hydrophobic colloids, on the other hand, are thermodynamically unstable. Since the energy input to disperse hydrophobic colloids is very high, the increased entropy does not compensate the enthalpy (ΔH). Therefore the increment of free energy of the system is positive.

$$\Delta G = \Delta H - T\Delta S > 0$$

The thermodynamically unstable hydrophobic colloidal particles maintain their stability through interactions (forces) at their surfaces. The nature of these forces, called colloid forces or colloid interactions, and their significance in treatment process is discussed in this chapter.

2.1.1. Particle surface charge and electrical double layer

Most particles in water possess an electrical charge, and the sign of the charge at neutral pH is usually negative (Nefhof and Loeb, 1972; Hunter and Liss, 1979). There are three important paths to the origin of surface charge (Frolov, 1982; Amirtharajah and O'Melia, 1990; Mørk, 1997).

First, surface groups on the solid may react with water and accept or donate protons (ionisation mechanism). A classical example is silica with surface silanol group ($\equiv$SiOH), which when coming into contact with water donates proton:

$$\equiv Si\text{-}OH + H_2O \Leftrightarrow \equiv Si\text{-}O^- + H_3O^+ \qquad eq.\ 2\text{-}1$$

In acidic conditions (pH<4) a silanol group accepts proton and the oxide charges positively:

$$\equiv \mathrm{Si\text{-}OH} + H_2O \Leftrightarrow \equiv \mathrm{Si\text{-}OH_2^{+}} + OH^{-} \qquad \text{eq. 2-2}$$

The second mechanism involves adsorption of ions or molecules from the bulk phase. Thus, as a result of preferential adsorption of ions of electrolytes the surface can acquire charge. Once again it may be illustrated with the help of silica:

$$\equiv \mathrm{Si\text{-}OH} + Ca^{2+} \Leftrightarrow \equiv \mathrm{Si\text{-}OCa^{+}} + H^{+} \qquad \text{eq. 2-3}$$

$$\equiv \mathrm{Si\text{-}OH} + HPO_4^{2-} \Leftrightarrow \equiv \mathrm{Si\text{-}OPO_3H^{-}} + OH^{-} \qquad \text{eq. 2-4}$$

In the municipal wastewater environment colloids can acquire charge by adsorption of surfactant, this may be illustrated as follows:

$$xR\text{-}OSO_3^{-}+(Me_yO_z\cdot nH_2O)_m \Leftrightarrow (Me_yO_z\cdot nH_2O)_m\cdot x[R\text{-}OSO_3^{-}] \qquad \text{eq. 2-5}$$

The hydrophobic part of the surfactant molecule adsorbs on the surface of colloidal particle, and the hydrophilic part of the surfactant is directed to the water phase (Pushkarev and Trofimov, 1975).

There are substances that are unable to exchange or adsorb ions. Such particles acquire their charge due to orientation of polar molecules on the surface (the third mechanism). The charge sign depends on the dielectric properties of the both phases, positively charges the phase with greater dielectric permittivity. Since the dielectric constant of water is very high most of the substances in water are negatively charged.

Charged particles affect the distribution of surrounding ions in the media in such a way that ions with opposite charge are concentrated around charged particle. Together with Brownian motion this leads to the formation of so called electric double layer. Fig. 2.1 shows schematically a negatively charged colloidal particle with cloud of ions (double layer) around the particle. The modern concept of double layer formation is based on the Stern model (Stern, 1924). Schematically the Stern model is shown in Fig. 2.2. According to this model the layer of counterions consists of two parts:

The Stern layer (or the inner part) is formed by ions, which are specifically adsorbed on the charged surface. The Stern plane divides the Stern layer into the inner Helmholtz plane and the outer Helmholtz plane (Hunter, 1987). The distance from the surface to the Stern plane is about the radii of hydrated ions, which form double layer (δ).

The Gouy-Chapman layer (or the diffuse layer) expands from $x = \delta$ to λ. The thickness of the diffuse layer (λ) is determined by the properties and composition of the colloidal system. According to accepted concepts the electric potential in the Stern plane decreases linearly up till potential of diffuse layer and so exponentially.

When an electric potential is applied across a suspension of negatively charged particles, they move towards the positive electrode. The potential that causes the motion of the particles is associated with the plane of shear of fluid around the particles and is called zeta (ζ) potential or electrokinetic potential. The exact location of this slipping plane has been discussed for decades. Lyklema (1978) locates the slipping plane at the outer border of the Stern layer. The zeta potential is an indirect measurements of the charge of particles and can be obtained from the number of electrokinetic techniques (Hunter, 1981).

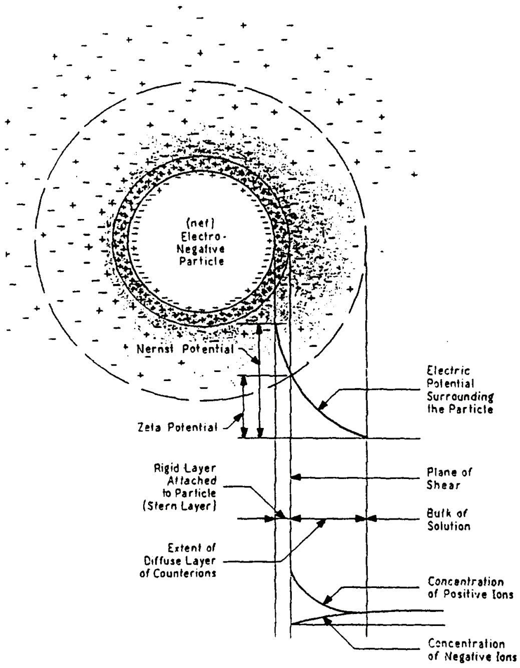


Fig. 2.1. Negatively charged particle, double layer and the location of the ζ-potential (After Amirtharajah and O'Melia, 1990).

from clear though some researchers focused on the subject (Lu and Song, 1991). The attachment of bubbles to particles is of crucial importance in the flotation of minerals and is governed by hydrophobic interactions (Veitser and Mints, 1984; Lu, 1991).

Polymer bridging. Long-chain polymers adsorb on particles and with large adsorbed amount can cause steric stabilisation as discussed above. With much less adsorbed polymer, an individual chain can become attached to two or more particles, thus ”bridging” them together. In this way particles can form aggregates even though they may be charged and repel each other. This effect is the basis for the utilisation of polymers in flocculation.

2.2. Characterization of polyelectrolytes and principles of their action as coagulants/flocculants

Organic macromolecules or polymers are made up of sub-units called monomers. A polymer build up of identical monomers is defined as a homopolymer. More complex macromolecules that consist of more than one monomer are known as copolymers.

The polymers used in water and wastewater treatment are water-soluble, in solution they have flexible chain structures. The simplest primary structure of such molecules is a linear chain of atoms connected by chemical bonds. By rotation about the bonds, the molecule changes its shape (or conformation). The fact that polymer chains may be linear, branched, or cross-linked adds to their complexity.

There are several types of polymers used in water and wastewater treatment. It is possible to distinguish between natural macromolecules (biopolymers), synthetic macromolecules, and chemically modified biopolymers.

The natural and chemically modified natural polymers used in water and waste treatment systems include starches, galactomannanas, cellulose derivatives, microbial polysacharrides, gelatines, and chitosan. These are water-soluble polymers, mainly nonionic, but cationic and anionic modifications may be obtained.

Synthetic organic polyelectrolytes are widely used in water and waste water treatment processes. Today there are thousands of commercially available polymeric products, but the number of active compounds (or types of compounds) is not as large as the number of products. Some of the most used polymers are presented in
Table 2.1.

Table 2.1. Synthetic organic polymers used in water and wastewater treatment.

Common name and abbreviation	**Chemical structure**	**Type**
Acrylamide polymers Polyacrylamide(PAM)	$(C_3H_5NO)_n$	Nonionic
Acrylamide- Acrylic acid copolymer	$(C_3H_5NO \bullet C_3H_4O_2)_n$	Anionic
Diallyldimethyl ammonium chloride, homopolymer (PDADMAC)	$(C_8H_{16}N \bullet Cl)_n$	Cationic
Epiclorohydrin-dimethylamine, copolymer (P-Epi-DMA)	$(C_5H_{12}ON \bullet Cl)_n$	Cationic
Polyethylenimine (PEI)	$(C_2H_5N)_n$	Cationic

2.2.1. Polymer chemistry

There appears to be some inconsistency in approaches to classification of polymer chemistry, particularly between US and European systems, and to some extent the systems adapted by individual companies.

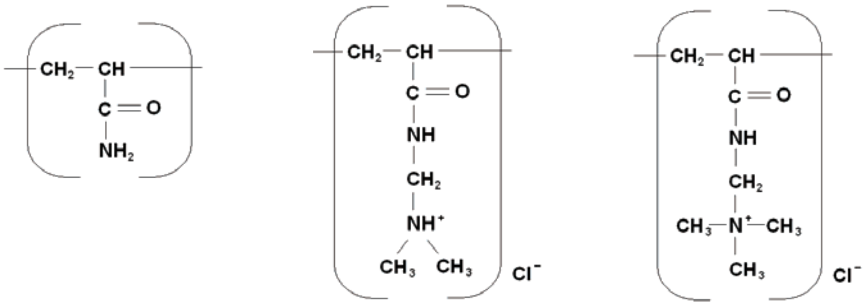
US adopt the nomenclature of the Synthetic Organic Chemical Manufactures Association (SOGMA). SOGMA defines the three major polymer chemistries as belonging to classes 1a (polyacrylamides), 2a (PDADMACs) and 6a (epichlorohydrin-amine) (Nalco, 1995). However, the terminology used to describe these flocculants is somewhat loosely applied in the water treatment industry, particularly in relation to PDADMAC and epichlorohydrin-dimethylamine classes. The terms “cationic polyamine”, “quaternary polyamine” and “poly-quaternary amine” are used somewhat interchangeably to present either of above mentioned classes. As such, these terms cannot be used to reliably identify flocculant chemistry.

Although there are a wide variety of possible chemistries, which can be used to prepare polyelectrolyte flocculants, there are only three significant classes of flocculant chemistry that dominate in the water treatment field. These are Polyacrylamides, PDADMACs and P-Epi-DMAs.

Polyacrylamides

Perhaps the most common chemistry for flocculants is that based upon polyacrylamide (PAM). Polyacrylamide is non-ionic polymer, but may be modified to be both anionic and cationic. Cationic polyacrylamides are usually prepared by co-polymerisation of acrylamide (structure (a) with a quaternary ammonium derivative of acrylamide. Most cationic polyacrylamides tend to have high molecular weights (ca. 10^7 Daltons), with charge density varying from low to high depending upon application. Structures (b) and (c) in Fig. 2.5 illustrate cationic acrylamide-based polymers. Structure (b) depicts the tertiary amine group, which may be quaternised to give the structure (c) (Fig. 2.5).

Structures (b) and (c) exemplify monomers that can be co-polymerised with acrylamide (a) to create a variety of copolymers. Though related, these exhibit somewhat differing properties based on their monomer characteristics and on the manner in which the co-polymerisation reaction takes place.



(a) (b) (c)

Fig. 2.5. Structures of Polyacrylamides (PAM).

Poly-DADMACs

The class of polyelectrolytes commonly known as Poly-DADMACs (PDADMAC) are polymers of diallyldimethyl ammonium chloride (DADMAC). The PDADMAC flocculant is a water soluble polyelectrolyte of low to medium molecular weight and 100% charge density. The structure of DADMAC monomer is presented in Fig. 2.6

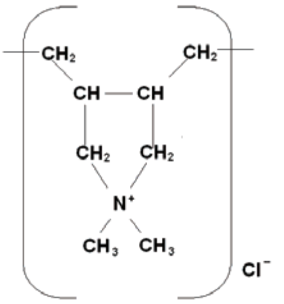


Fig. 2.6. Structure of poly-DADMAC (PDADMAC).

Co-polymerization of DADMAC with acrylamide allows obtaining high molecular weight PDADMACs. As the cationic charge is only carried in the quanternary nitrogen of the pyrrolidinium ring, the degree of charge density can be controlled to some degree by manipulation of the proportion of component monomers. Typically the flocculant may contain 15-50% w/w active polymer along with water, catalyst and residuals from the manufacturing process.

Polyamines

Polyamines (P-Epi-DMA) are polyelectrolytes prepared by the polymerisation of epichlorohydrin with primary amines or secondary amines. The dominating product in this class is co-polymer with dimethylamine (secondary amine). Epichlorohydrin-dimethylamine flocculants tend to have a relatively lower molecular weight ($<10^6$), with the high charge density arising from the quaternary amine nitrogen residing on the linear backbone of the polymer.

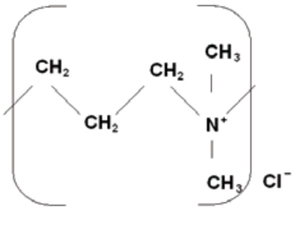


Fig. 2.7. Structure of polyamine (P-Epi-DMA).

2.2.2. The charge of polyelectrolyte

The polymers which, when dissolved in a polar solvent (generally water) acquire a large number of elementary charges distributed along the macromolecular chain are classified as polyelectrolytes.

According to charge sign polyelectrolytes may be divided on four groups. Polymers that possess positive charge are called cationic and those that possess negative charge are called anionic. Polymers with no charged groups or with very low tendency to develop them in aqueous solution are known as non-ionic polymers. Non-ionic polymers are not polyelectrolytes according to the strictest chemical definition, but the term is still used. There are so called ampholyte polymers that have both positively and negatively charged groups on the same chain. At the present time, it is believed that the polyampholytes have little utility for water treatment. While cationic, anionic and non-ionic polymers are widely used. Cationic polyalectrolytes are often referred as primary coagulants, while non-ionic and anionic polyelectrolytes are referred as coagulant aids or flocculants.

Charge density that is a number of charged groups per monomer unit of the polymer, is an important characteristic for polyelectrolytes (Fleer *et al.*, 1993). Charge density is often presented as a mole fraction (mole %) that is the amount of mole of charged monomer divided by total mole of monomers in the macromolecule.

The charge of polyelectrolyte may be pH dependent that allows division onto weak and strong polyelectrolytes. The weak polyelectrolytes acquire charge during ionisation reaction and the overall charge on the molecule depends on pH and ionic strength of the media. Most of the polyelectrolytes used in water and wastewater treatment are weak polyelectrolytes, which carry weakly acidic (e.g., carboxylic) or basic (e.g., amino) groups. If the polymer charge is an essential aspect of its functioning, it is important to know the pH range over each the charge is maintained. Fig. 2.8 shows the typical trend of ionic charge for cationic polymers as a function of pH. Three types of polyacrylamide polymers and one PDADMAC are shown. This indicates the distinction between a Mannich polymer, which deprotonates at high pH and a comparable polymer that has been 85% quaternised and between completely quaternised PDADMAC and a copolymer of acrylamide that is nearly all quaternised, but has a 55 mole % charge content. The data presented indicate that Mannich polymer charge is highly pH dependent unless quaternised, and then slightly so. Both quaternised polymers, PDADMAC and quaternised copolymer of acrylamide, maintain constant charge.

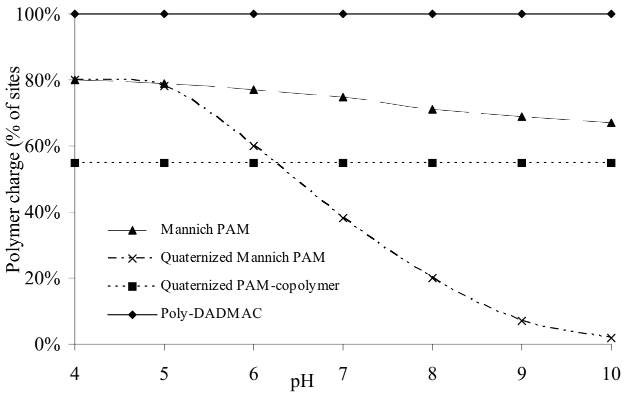


Fig. 2.8. Charge trends typifying various types of cationic polymers.

2.2.3. Size of macromolecule

Molecular weight is a common characteristic of the polyelectrolyte. Because polymerisation reactions are totally random, molecular weight (MW) for polymeric compounds represents an average with a Gaussian distribution. MWs for water treatment polymers are best measured by light scattering or by ultracentrifugation. Viscosity can also be used as a gross estimate of MWs. In practice, most manufacturers have used light scattering during product development and scale-up coupled with viscosity measurements. Since light scattering is very equipment and operator intensive, it is not used for routine quality control. Once a polymer is in full-scale production, viscosity correlated back to the original light scattering data is used to estimate MW. The following equation is used to correlate insintric viscosity of the polymer to its molecular weight:

$$[\eta]=K\ (MW)a,$$

where K and a are empirical coefficients.

The chart below lists the generally accepted terminology with regard to MWs in liquid/solids separation applications (actual ranges may vary from source to source or company to company).

Flocculants have relatively high molecular weight, perhaps 10 times or more than that of the typical primary coagulant polymers. As will be shown later, molecular weight and charge density of the polyelectrolytes have significant influence on the mechanism of colloid destabilisation.

Table 2.2. Classification of polyelectrolytes according to molecular weight.

Molecular weight range	**Classification**
<100.000	Low
100.000 – 250.000	Low-medium
250.000 – 1.000.000	Medium
1.000.000 – 5.000.000	Medium-high
5.000.000 – 10.000.000	High
>10.000.000	Very high

2.2.4. Contaminants and impurities in polyelectrolytes

It is important to realise that synthetic, water-soluble organic polymers have the advantage of low residuals. Nevertheless there is some residual polymer in treated waters that may enter the environment. Besides the polymer, there are always other substances introduced into water or wastewater together with the polymer, such as monomers, emulgating chemicals, oils and additives. Letterman and Pero, 1990 have thoroughly reviewed the chemistry of polyelectrolyte coagulant products sold for use in the water treatment field, including polymers, residual monomers and other product contaminants. Table 2.3 shows the contaminants that are known to be or may be present in synthetic polyelectrolytes. The contaminants presented in Table 2.3 are considered to be the most important impurities in polyelectrolytes used for the treatment of drinking water. In the table, “direct evidence” implies that the compound has been measured and its concentration in the polyelectrolyte has been reported in the literature. “Indirect evidence” implies that the determination of the compound was qualitative but not quantitative, and “speculative evidence” implies that the compound is used or possibly formed in the manufacture of the polyelectrolyte, but it is not certain whether it is present in the final product.

Table 2.3. Contaminants which may be present in synthetic polyelectrolytes (Pero, 1990).

Polyelectrolyte	**Contaminant**	**Evidence**
PAM	Acrylamide	Direct
	Hydroxypropionitrile	Direct
	Isobutyronitrile	Direct
P-Epi-DMA	Epichlorohydrin	Direct
	Glycidol	Direct
	1,3-dichloro-2-propanol	Direct
	1,2-dichloropropanol	
	3-chloro-1,2-propanediol	Direct
	2,3-dichloro-1-propanol	Direct
	Dimethylamine	Indirect
	2-hydroxy-3-dimethyl-aminopropyl chloride	Speculative
	1,3-Bil(dimethylamino)-2-propanol	Speculative
PDADMAC	Diallyldimethyl ammonium chloride	Direct
	Dimethylamine	Indirect
	Diallyl ether	Speculative
	Allyl chloride	Speculative
	5 Hexanal	Speculative

2.2.5. Analysis of polyelectrolytes

Despite the existence of limits on the amount of polyelectrolyte that may be used in the treatment of drinking water, little information exists on polyelectrolyte concentrations in the treated water or in the environment. This is mainly because the analysis of polyelectrolytes is difficult analytical problem, and although many attempts have been made to resolve it, no suitable method has yet emerged.

Colloid titration

When polyelectrolytes of opposite charge interacts they form strong stoichiometric complexes, which precipitate when the charges are neutralised. This is the principle of the colloid titration technique; the polyelectrolyte is titrated with an oppositely charged polymer and the end point is detected visually or spectrophotometrically, by turbidimetry or conductivity, or by using a charge detector.

This method is unable to differentiate between different types of polyelectrolyte and is subject to interference from other sample components including natural colour causing compounds and calcium. For this reason, colloid titration is not the method of choice. A limit of detection of 1mg/l has been quoted for cationic polyelectrolytes (Wang and Langley, 1977).

Lindquist & Straton's (1976) flocculation results indicated that the relative importance between polymer bridging and electrostatic considerations is pH dependent. At pH 9 and greater, polymer bridging is the dominant mechanism, while at pH less than 9, a charge interaction between polyethylenemine and colloidal silica is the dominant consideration. The effect of matrix, molecular mass, and ionic value of polymers on their interaction with suspended solids and dissolved organic matter were studied by Lurie & Rebhun (1997). They observed significant differences in interaction of the low molecular weight polymers and high molecular mass polymers with particles in the presence of soluble organic. The results claim that high molecular weight cationic copolymers of polyacrylamide flocculate suspended solids through "bridging", while "charge patch" flocculation was dominant mechanism for the low molecular mass polymers.

3. OBJECTIVES AND HYPOTHESES

The main objective of this work is to find ways to optimize the use of polyelectrolytes in wastewater treatment. This includes determination of polyelectrolyte interaction mechanism with colloids and particles in wastewater; identification of factors influencing coagulation and modeling the coagulation- flocculation with cationic polyelectrolyte.

- In spite of the fact that quite a few studies have been focused on wastewater treatment with polyelectrolyte some aspects of polyelectrolyte action are not fully covered and understood:
- There are few studies comparing a broad range of polyelectrolyte types and describing the effect of polyelectrolyte properties on colloid and particle destabilization and removal.
- A limited number of studies have been investigated the interplay between colloids and dissolved organic matter with respect to coagulation with polyelectrolyte.
- There is an indication that combined use of low dosage inorganic coagulant and cationic organic polyelectrolyte have synergetic effect on removal of colloids and particles.
- The relationship between coagulation and flocculation of wastewater colloids with polyelectrolytes is poorly covered.
- Few studies have been focused on documentation of residual polyelectrolyte concentration.

There are some questions, which need to be answered in order to achieve the objective of this work. The data presented in the literature review indicate that interplay between wastewater characteristics and polyelectrolyte chemical and colloidal properties influences the outcome of the coagulation-flocculation with polyelectrolytes.

Therefore, based on the literature review the following hypotheses arose:

Hypothesis 1.

The quality of raw wastewater, especially SS and COD concentrations, greatly effects polyelectrolyte consumption and treatment efficiency. Polyelectrolyte dosage and treatment efficiency can be predicted based on raw water quality parameters as turbidity, suspended solids concentration and COD.

Hypothesis 2.

Soluble organic matter may negatively effect the coagulation flocculation, leading to higher polyelectrolyte dosages and poor treated water quality.

Hypothesis 3.

The amount of charge is a key factor governing coagulation-flocculation i.e. the differences observed in the action of different polyelectrolytes at the same dosage are due to the different amount of charge introduced.

Hypothesis 4.

The molecular weight of polyelectrolyte is an important polyelectrolyte characteristic to ensure flocculation and particle separation. Medium to high molecular weight polyelectrolytes produce settable floc.

Hypothesis 5.

Combined use of low dosage of inorganic coagulant and polyelectrolyte may give good particle removal accompanied by a phosphate removal and low sludge production.

Hypothesis 6.

Polyelectrolytes may interact with soluble organic matter producing tiny unsettleable floc and changing the particle size distribution in coagulation with polyelectrolytes.

Hypothesis 7.

At the optimum conditions (optimum dose, mixing and flocculation) the residual polyelectrolyte concentration is minimal.

4. EXPERIMENTAL PROCEDURE

This chapter includes the description of the procedures and the techniques involved in experiments. The general characterisation of the municipal wastewater is given with special focus on the wastewater characteristics that affect treatability. The separate section is devoted to description of the procedure development for determination of the residual polyelectrolyte.

4.1. Methods

4.1.1. JAR-test procedure

Jar test procedure was used in the experiments. The flocculation vessels were 1 liter beakers and the suspension was mixed by a two-blade paddle stirrer (Flocculator Kemira, Sweden). Coagulant dosing was followed by intensive mixing to ensure as uniform mixing of the coagulant as possible. After mixing suspension was flocculated and settled.

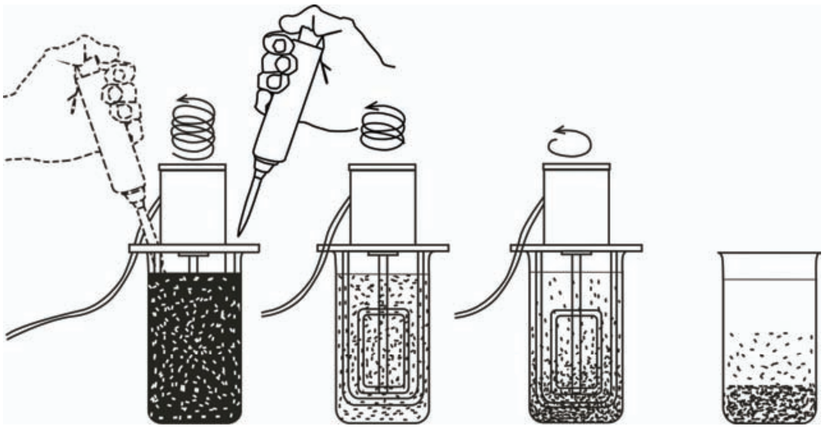


Fig. 4.1. JAR-test setup.

4.1.2. Standard analyses

Turbidity and SS were analysed according to Standard methods (1995). Chemical Oxygen Demand (COD) was analysed in a cuvette test (Dr. Lange's method, LCK114 and LCK 314). COD was determined from unfiltered samples, while samples for COD_f were filtered through a 1.2 µm Millipore filter (GF/C) before analysing.

4.1.3. Zeta-potential determination

The zeta-potential of the particles was measured with the laser diffraction apparatus COULTER DELSA 440SX. The DELSA 440 SX analyses data from four scattering angles. The simultaneous multi-angle analysis simplifies interpretation of the data. It also distinguishes between the particle charge heterogeneity and the diffusion effects over a wide range of particle sizes. The instrument is automated and provides a simple analysis, which can detect small charges in zeta-potential.

The method on which the measurements are based is called the Laser Doppler Velocimetry (LDV). The LDV is a method for measuring the speed of small particles. When the particles are suspended in a fluid in the presence of the known electric field, the velocity measurement is a measure of the mobility of the particles. For the majority of samples, the mobility is directly related to the zeta-potential of the particles. The LDV is analogous to the speed measurements of cars made by a radar. The small particles suspended in the fluid are illuminated by the laser beam. The light scattered to various angles is compared to the light in the reference beam to determine the Doppler shift of the scattered light. The Doppler shift of the light depends on the speed of the particles and the angle of measurement.

By making four independent simultaneous measurements at four angles, the COULTER ® DELSA 440SX provides validation of the mobility peaks.

By the trial-and-error method the following procedure was established for the zeta-potential measurements of the coagulated particles:

- The measurement of the zeta-potential was performed right after the rapid mixing step of the jar test, before any floc aggregation occurred.
- The pH was adjusted, if the difference from sample to sample was more than 0.2 units of pH.
- If the conductivity of the sample was in a range of 0.5ms/cm, the current mode was used (current between 0.5 and 5mA in most cases gave the best results). In the case of sample with low conductivity (< 0.1ms/cm), the voltage mode was applied (often 300mV was the only field allow getting any results).

4.1.4. Monitoring of the floc growth

The experimental set-up adapted from Gregory and Nelson (1986) is shown schematically in Fig. 4.2. The flocculating suspension was pumped through transparent tube of 3mm internal diameter at a rate of about 20ml/min. The sample was monitored continuously by a Photometric Dispersion Analyser (PDA 2000, Rank Bros.Ltd., Cambridge, UK). The sample was returned to the flocculation vessel after passing through the monitor. In order to avoid possible problems of the floc break-up the peristaltic pump was located after the monitor.

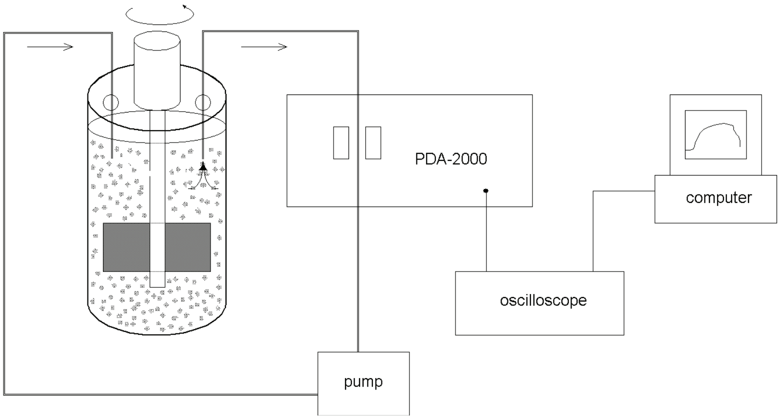


Fig. 4.2. Schematic diagram of experimental set-up.

Fundamental principles of the technique

The technique is developed at University College, London and described by Gregory (Gregory and Nelson, 1986). The suspension flows through an optical cell via a transparent tube, and is illuminated by a narrow beam of light perpendicular to the direction of flow. The intensity of transmitted light is monitored by a photodetector. The output of the photodetector is converted to a voltage, which consists of a steady (DC) component and a fluctuating (AC) component. The steady component is a measure of the average transmitted light intensity and depends on the turbidity of the suspension. The AC component arises from random variations in the number of particles in the sample. Because the suspension flows through the cell, the actual sample in the light beam is continually being renewed and local variations in particle number concentration give fluctuations in the transmitted light intensity. These fluctuations cease when the flow is stopped. The root mean square (RMS) value of the fluctuating (AC) signal is related to the average number concentration and size of the suspended particles. The RMS value of the fluctuating signal increases, when aggregation of particles occurs.

In order to eliminate the effect of drift, the RMS value is divided by the steady (DC) value to give a ratio, R (RMS/DC). This value remains essentially unaffected by contamination of the optical surfaces or electronic drift (Gregory and Nelson, 1986).

It can be shown that R depends on the concentration and the size of the suspended particles, as well as on the dimensions of the illuminated sample volume. For the general case of a heterodisperse suspension, the ratio value is given by eq. 4-1:

$$R = (L/A)^{1/2}\left(\sum N_i C_i^2\right)^{1/2} \quad \text{(Gregory and Nelson, 1986).} \qquad \textit{eq. 4-1}$$

where L is the optical path length and A is the effective cross-sectional area of the light beam. The sum is taken over all types of particle i, with number concentration N_i and light scattering cross-section C_i (which depends on the size and shape of the particles). The nature of the sum in eq. 4-1 is such that smaller particles contribute relatively little to the ratio value and that, in an aggregating system the larger aggregates have a greater influence on R (Gregory and Nelson, 1986).

4.1.5. Particle size determination

Particle size was measured using a Beckman-COULTER LS 230 laser particle size analyser, equipped with a fluid modul. The LS 230 measures particle sizes from 40 nm to 2000 µm by laser difraction. It is based on the principle that particles scatter and diffract light at certain angles based on their size, shape, and optical properties.

Conventional (Fraunhofer) laser diffraction is used to measure particles in the size range 0.4 µm to 2 mm. The Fraunhofer theory relies on the fact that when light from a laser is shining at a particle, some of it is diffracted. The amount of diffraction is dependent upon the size of the particle. The smaller the particle, the greater the maximum angle of diffraction. Thus, particles of different sizes each produce a characteristic diffraction pattern.

Polarisation Intensity Differantial Scatter (PIDS) is used to measure particle size down to 0.04 µm. This is also based on laser diffraction, but measures light flux only at high angles to the beam. Using six detectors and a tungsten light source, the PIDS unit compares the intensity of light scatter at two polarisation angles, at different wavelengths (450, 600 and 900 nm) (Coulter Corporation, 1994).

The LS 230 applies a user-specified optical model to interpolate a continuous particle size distribution from the signals from each particle in the sample. The Fraunhofer model, based on the Fraunhofer theory of light scattering was used for interpolation. This model does not require a prior knowledge of the optical properties of the sample. Interpolation of the LS 230 output was carried out using version 3.0 of the Coulter LS Control software.

4.1.6. Determination of residual polyelectrolyte

Two methods were adopted to determine the concentration of residual polyelectrolyte in coagulated wastewater. The eosin complex formation was used for determination of polyelectrolytes containing quaternary ammonium. The colloid titration method is not chemistry specific and can be used for determination any polycation.

Eosin complex formation method

The method of polyelectrolyte determination described by Furlong and Elliker (1953) was adopted for quantifying the residual polyelectrolyte in the treated sewage. The method is based on formation of a coloured complex between the quaternary ammonium group of polymer and tetrabrom fluorescein (eosin). The optimum pH for complex formation is 3.4 to 3.6. The method is specific for the polyelectrolytes that possess a quaternary ammonium group. Since determination of polyelectrolyte was reported to be affected by the colour and proteins (Klyachko *et al.*, 1984), an initial study of the absorbance spectra was undertaken.

A Standard curve was generated by adding a known dose of polyelectrolyte to the clarified sewage. A 5ml of the buffer was added to a 5ml of the sewage spiked with polyelectrolyte, followed by addition of 0.5ml of 0.05% eosin solution and the spectrophotometric measurements were undertaken in the wavelength range 450 – 600nm. This process was repeated several times for at least 5 different polyelectrolyte concentrations and a blank.

Fig. 4.3 shows that the absorbance spectra of eosin and eosin/PDADMAC complex in the wastewater overlapping. Therefore, the determination cannot be carried out at the wavelength giving the maximal absorbance, but an optimal wavelength should be chosen giving maximal difference (ΔA) in absorbance of eosin and complex.

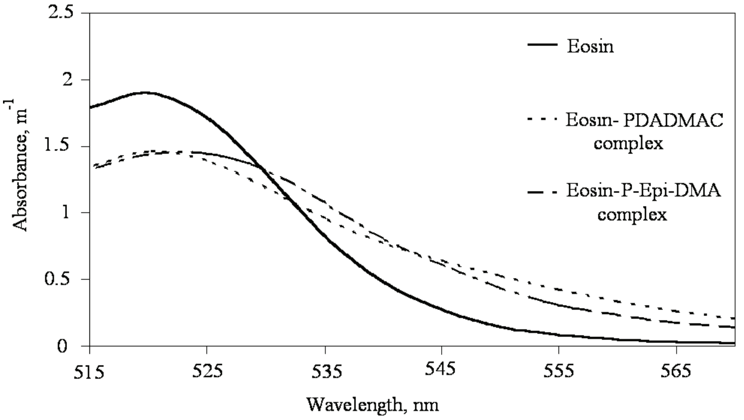


Fig. 4.3. Absorbance spectra of eosin and eosin-polyelectrolyte complexes.

In order to find the optimal wavelength (λ_{opt}) the absorbance data was plotted against polyelectrolyte concentration as Fig. 4.4 illustrates. The maximum slope of the curve was observed at 550nm and the Beer-Lambert law was valid for the eosin/PDADMAC complex at this wavelength.

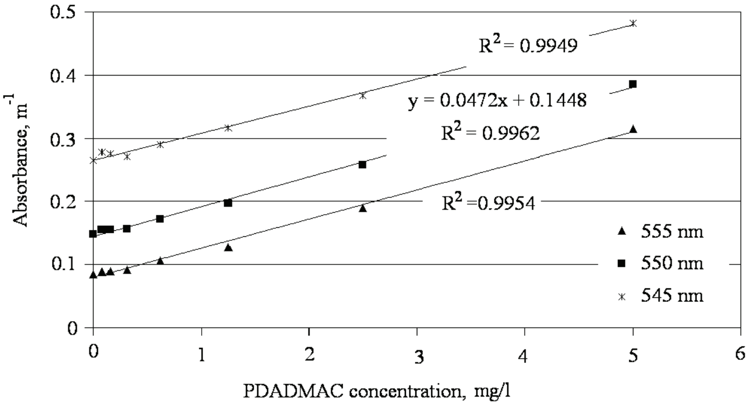


Fig. 4.4. Calibration curves showing the validity of Beer's law for eosin-PDADMAC complex.

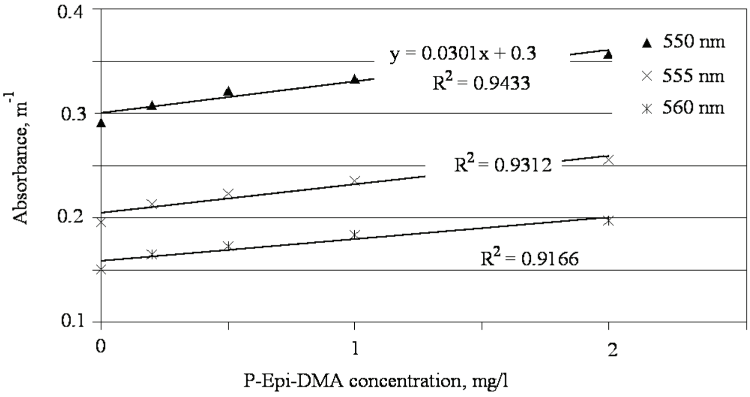


Fig. 4.5. Calibration curves showing the validity of Beer's law for eosin-poly-Epi-DMA complex.

Since the Beer-Lambert law is valid, the simple method, called "method of additions" can be used to avoid influence of the wastewater impurities, such as colour, turbidity and proteins, on the determination of the residual polyelectrolyte. The method of additions is based on comparison of absorbance of the analysed sample and the absorbance of the same sample spiked with known amount of the analysed compound. The concentration of the compound can be determined from the following equation:

$$C_x = C_a \frac{D_x}{D_{x+a} - D_x}, \qquad eq.\ 4\text{-}2$$

where C_x is the amount of polyelectrolyte in the sample (mg), C_a is the added amount of polyelectrolyte (spike) (mg), D_x is the absorbance of the sample and D_{x+a} is the absorbance of the spiked sample.

The absorbance range in our experiments was lower than the optimal absorbance generally recommended in the spectrophotometric literature. The error curve was generated in order to estimate reliability of the results. This curve is shown in Fig. 4.6. At polymer concentration from 0.1mg/l to 1mg/l, that corresponds to absorbance in the range 0.03 – 0.06, the error is 3%.

The following procedure was developed for determination of the residual polyelectrolyte:

- 5ml of unknown sample was spiked with polymer to give difference in absorbance (D_{x+a}-D_x) ≥ 0.1.
- 5ml of buffer were added to the unknown sample and to the spike, followed by addition of eosin solution (0.5ml).
- Absorbance was measured 3-5 minutes after addition of eosin, as recommended by Klyachko *et al.* (1984), at a wavelength of 550nm, using 5cm cuvette. The concentration of the polyelectrolyte in the sample was calculated according to the eq. 4-2.

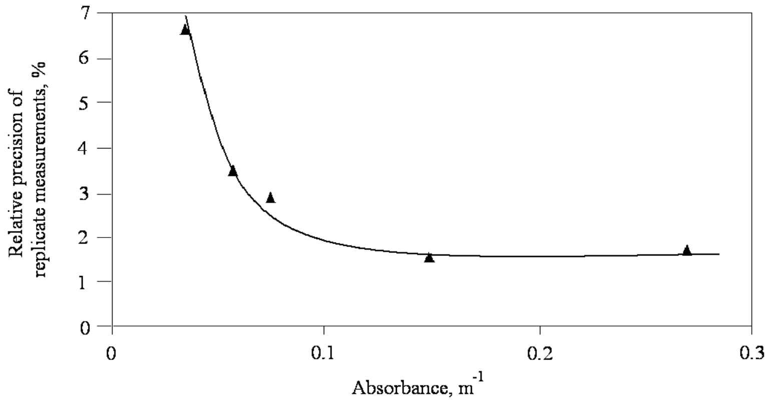


Fig. 4.6. Error in spectrophotometric measurements as a function of absorbance.

Colloid titration method

The colloid titration method was adopted for determination of the residual concentration of poly-acrylamides and poly-ethylenimines. The procedure used by Becker *et al.* (2000) was adopted. The detailed description of the procedure was kindly provided by Becker (2001).

Clarified sewage was used for generation of the standard curve, as it is important to keep the solution chemistry in the standard curve tests and that of the test samples the same. Using clarified sewage ensures that any effects from variations in the ionic strength of the solution, the amount of residual organic material etc, was minimised. Therefore, the standard curve and all results derived from the standard curve were obtained from the same raw sewage source with a minimal time delay.

The standard curves were generated by adding a known dose of polyelectrolyte to clarified sewage (90ml) and then adding Bolin Clay (2g/l, Merck Bole white powder, kaolin) suspension (10ml of a 20g/l of clay in DI water). The mixture was stirred for 30 sec at 400 rpm, then flocculated for 2 min at 100 rpm and allowed to settle for 5 minutes before the top 30ml of solution was withdrawn for turbidity analysis. This process was repeated several times for at least 5 different polyelectrolyte doses and a blank. A graph of turbidity versus polyelectrolyte dose was then plotted.

The method was sensitive to polyelectrolyte type. The detection limit varied between 0.5 and 2.0mg/l.

The test method was the same as used to generate the standard curve. A Bolin Clay (2g/l, Merck Bole white powder, kaolin) suspension (10ml of a 20g/l of clay in DI water) was added to 90 ml of the settled supernatant test sample and mixed at 400 rpm for 30 seconds, before reducing the speed to 100 rpm for a further 3 min to facilitate the maturation of the flocs. The flocculated mixture was then allowed to settle for 5 minutes before the top 30ml of solution was withdrawn for turbidity analysis.

This process was repeated with appropriate dilutions (with clarified sewage) until the turbidity result fell into the sensitive region of the standard graph (200 to 500 NTU). An effective residual polyelectrolyte concentration was then determined from the standard graph of turbidity versus polyelectrolyte, which when multiplied by the dilution factor, gave an estimated residual polyelectrolyte concentration.

4.2. Materials

4.2.1. Coagulants

Based on the reviewed literature the cationic polyelectrolytes were considered to be the most suitable coagulants for the application in this study. Therefore, a number of cationic polyelectrolytes were tested as primary coagulants for the municipal wastewater. The polyelectrolytes were applied as the only coagulant and in combination with a low dosage of inorganic salt.

As an inorganic coagulant, a product (JKL) from Kemira Chemicals AS was used. The JKL is a Ferric Chloride Sulfate containing 11.6% of Fe^{3+}.

Poly-acrylamides, Poly-ethylenimine, P-Epi-DMAs and PDADMACs of different charge densities and molecular weights were tested as the only coagulants and in combination with the JKL. These four types of polyelectrolytes were chosen, since they are extensively used in the water and wastewater treatment. Since colloids in the municipal wastewater are negatively charged, only the cationic polyelectrolytes were applied as primary coagulants.

The characteristics of the polyelectrolytes were chosen to provide the best coverage of the products available on the market and to allow the comparison of the different polyelectrolytes. The molecular weight of the polyelectrolytes used varies from 10 000 to 12 000 000 Dalton and the charge density varies from 0.1 to 7 meq/g. The polyelectrolytes with a molecular weight lower than 10 000 were not included in the experiments since they are known as stabilisers rather than coagulants.

The polyelectrolytes were divided into two groups according to their molecular weight: the low molecular weight group and the high molecular weight group. The group of the low molecular weight polyelectrolytes includes the poly-Amines and the PDADMACs, with molecular weights up to 1 200 000g/mol. The group of the high molecular weight polyelectrolytes includes the poly-acrylamides and the poly-ethilenemines with molecular weights from 2 000 000g/mol and upwards.

Both the poly-amines and the PDADMACs are homopolymers, as was discussed in chapter II, and therefore the charge density cannot be varied. The characteristics of the polyelectrolytes used in the experimental investigation are given in Table 4.1.

Table 4.1. Polyelectrolytes applied in research as primary coagulants.

Polyelectrolyte code	**Type**	**Charge, %**	**Molecular weight**
$PA_{10^{*},\,100^{**}}$	Poly-Epi-DMA	100	10 000
$PA_{400,100}$		100	400 000
$PA_{800,\,100}$		100	800 000
$PA_{100,\,100}$		100	100 000
$PAM_{4000,70}$	Copolymers of Polyacrylamide	70	4 000 000
$PAM_{10000,70}$		70	10 000 000
$PAM_{10000,40}$		40	10 000 000
$PE_{10000,70}$	Poly-Ethilenimine	70	10 000 000
$PE_{12000,70}$		70	12 000 000
$PD_{400,\,100}$	PDADMAC	100	400 000
$PD_{800,\,100}$		100	800 000
$PD_{1200,\,100}$		100	1 200 000
$PD_{250,\,100}$		100	250 000
$PD_{100,\,100}$		100	100 000

* - Molecular weight in thousands
** - Charge density in %

4.2.2. Wastewater

The wastewater used in the experiments was sewage from the two municipal wastewater plants of Trondheim and from the NTNU's research hall with sewage from the neighboring households. The composition of the wastewater varied significantly with both place and time. This was partly due to variations in the discharged amounts of substances. However, the main reason was the variation in the water consumption (the day-time variations) and the weather conditions. The treatability of the wastewater varied with variation of the wastewater quality and was determined by the amount of impurities and their chemical and physico-chemical properties.

As was thoroughly discussed in Chapter I, classified by the size, the wastewater impurities can be particulate, colloidal or soluble (dissolved) matter. In natural systems, like wastewater, particles of all sizes are present, and the particle size distribution is a continuous function. Fig. 4.7 illustrates the particle size distribution in the municipal wastewater. Curve 1 represents the wastewater obtained from the NTNU's research hall, curve 2 represents the wastewater from the Høvringen wastewater treatment plant. The results represent the distribution of the volume of the particles with reference to their diameters. It is important to remember that a given volume of a particle with a small particle diameter represents a much higher number of particles than the same volume of particles with a higher particle diameter. The particle size distribution is a very important parameter for characterisation of treatability of the wastewater (Adin, 1999). The comparison of the two curves presented in Fig. 4.7 can provide information about treatability of both wastewater samples.

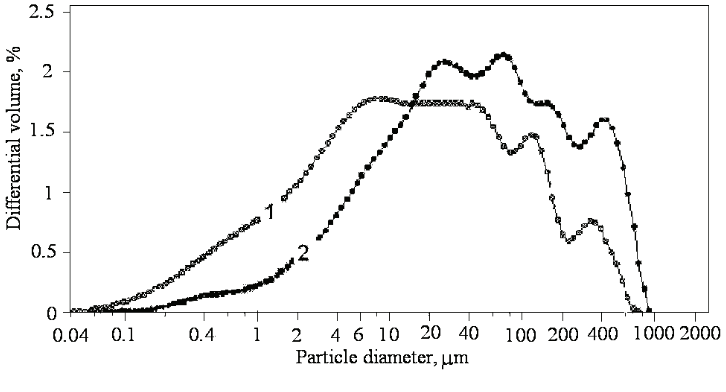


Fig. 4.7. Particle size distribution in raw sewage from /NTNU research hall (1) and from Høvringen treatment plant (2).

As the curves illustrate, both wastewaters have a broad particle size distribution and contain an entire range of colloids from ultramicroparticles (from 1 to 100nm) to coarse-disperse particles (> 100μm). The wastewater sample obtained from NTNU research hall, unlike the sample from the Høvringen treatment plant, contains a large amount of the small particles (particle diameter < 0.4μm). Generally, a particle size distribution may be affected by the nature of the particles or by the flocculation conditions in the sewer system. Since the samples were taken in the same day with minimal time delay, the difference is most likely due to conditions in the sewer system (Hvited-Jakobsen *et al.*,1995; Ødegaard, 1997).

The systems containing a large number of small particles have a significant specific surface and, therefore, the excess of surface energy. Due to this such systems are thermodynamically unstable and tend to aggregate.
In a complex system like wastewater particles may decrease the surface energy, by adsorption of the polymeric component from the aquatic phase. The stability of such particles will be significant due to the steric stabilisation effect described above. Thus, a high dispersity of the wastewater may indicate that the treatability is low. For example, from the two samples illustrated in Fig. 4.7 the wastewater, represented by curve 1, is more difficult to coagulate (the higher dosages of coagulant should be applied).

A rough estimation of the particle size distribution can be made from the turbidity/suspended solids (SS) ratio. The correlation between the turbidity and the suspended solids (presented in Fig. 4.8) was obtained for wastewaters from the Høvringen treatment plant and NTNU research hall. The trend line for Høvringen data crosses the abscissa at the point 2,8 and this is the approximate amount of turbidity that is caused by very small particles, which come through the filter. The same value for the wastewater from NTNU research hall is 5,9. Therefore, the concentration of the small particles (<1µm) is larger in wastewater from NTNU research hall.

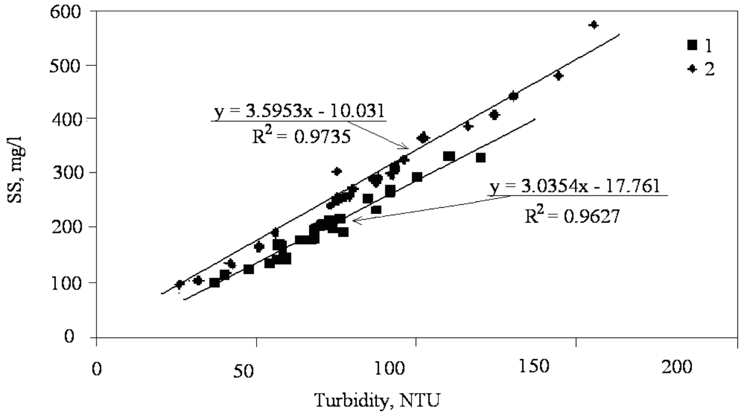


Fig. 4.8 .Correlation between turbidity and suspended solids for sewage from NTNU research hall (1) and from Høvringen treatment plant (2).

The concentration of particles in raw wastewater has a significant effect on the treatability of wastewater. It is well known that diluted systems are more difficult to destabilise due to the low probability of interaction between particle and polyelectrolyte. This lead to the poor aggregation of destabilised particles into larger flocs. The concentrated suspension, on the other hand, may exhibit a natural tendency to agglomerate. Therefore the role of polyelectrolyte is minimised to the initiator of this natural phenomenon.

In order to conduct the experiments with real sewage and at the same time be able to control certain parameters, the raw sewage was modified. In order to change the particle size distribution and provide source of SS, the raw sewage was fractionated in a cone settling tank as shown in Fig. 4.9. The settled solids were dosed to the raw sewage in order to change the SS concentration. This procedure allowed keeping COD$_f$ relatively constant.

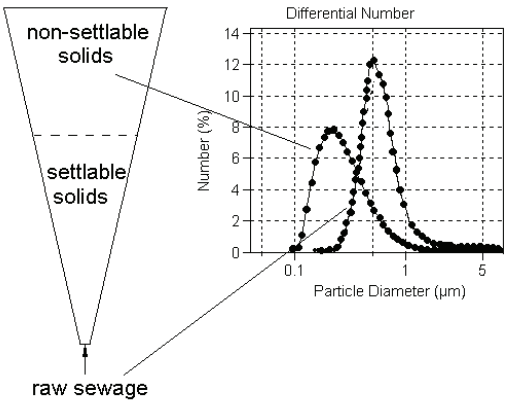


Fig. 4.9. Fractionation of raw sewage in a settling cone in order to manipulate particle size distribution.

The concentration of the filtered COD was also manipulated during the experiments by using primary sludge as a source for obtaining soluble organic matter. The primary sludge was first filtered through the glass-fibre filter (pore diameter 1µm) and then through the membrane filter (pore diameter 0,45µm). The filtrate was dosed it to the wastewater to increase the soluble COD content, while keeping COD$_f$ unchanged.

The characteristics of raw wastewater used in screening experiments are presented in Table 4.2. The characteristics of raw wastewater used in optimization experiments are presented in Table 4.3. In optimization experiments the raw wastewater was modified to produce wastewater with three levels of SS and COD$_f$ concentrations as was shown in Table 4.7. Therefore, nine modifications were obtained for each raw water.

Table 4.2. Wastewater used in screening experiments.

Wastewater	**Turbidity, NTU**	**SS, mg/l**	**COD, mg/l**	**COD$_f$, mg/l**
Raw water-01	55	186	167	61
Raw water-02	54	126	187	30
Raw water-03	60	178	155	49
Raw water-04	35	33	-	-

Table 4.3. Raw wastewater used in optimization experiments.

Wastewater	Turbidity, NTU	SS, mg/l	COD, mg/l	COD_f, mg/l
Raw Water 1	31	39	141	44
Raw Water 2	56	102	177	76
Raw Water 3	114	272	248	90
Raw Water 4	70	168	191	80

4.3. Experimental design

The coagulation experiments were divided into two phases. During the first phase, the primary goal was to decide what factors were of principal importance to the process by using factorial design statistics at two levels. During the second phase, the identified factors were investigated more thoroughly at three levels by using Box Behnken design statistics (Esbensen *et al.*, 2000).

At the initial stage of the study factorial design at two levels was used because it gives the possibility to investigate a great number of factors and their effect on a certain variable. With help of this design the directions for future experiments were determined. The factorial design at two levels implies that each factor is investigated at a low and a high level.

By performing factorial design the main effects and the interaction effects were identified. A main effect directly influence the result whereas an interaction effect implies that the effect of a variable can change as other variables are changed.

The software product Unscrambler v7.5 was used for generation and evaluation of factorial designs and Box Behnken designs.

The screening test was divided into two separate sets of experiments. Eight factors were selected. The investigated factors and their levels are presented in Table 4.4. One set of experiments was designed for low molecular weight polymers (PDADMACs and P-Epi-DMAs) and another for high molecular weight polymers (poly-Acrylamides and poly-Ethylenimines). This division was dictated by the software organisation (only two levels are possible in fractional factorial design in statistical package Unscrambler v 7.5). The resolution of the design was such that main effects were not confounded with each other and with two-variable interactions, but two-variable interactions were confounded with each other.

Table 4.4. Factors investigated in screening test.

Factor	Low level	High level
SS, mg/l	150	450
COD_f, mg/l	56	158
pH	6.5	7.5
Temperature, °C	6	15
Polymer type	PDADMAC	P-Epi-DMA
Molecular weight	400 000	800 000
Polymer dose, mg/l	1	5
JKL dose, mmol/l	0	0.2

Additional screening test was designed to investigate the effect of mixing and flocculation parameters. The investigated factors are presented in Table 4.5. The results of mixing and flocculation test will be discussed later in this chapter.

Table 4.5. Factors investigated in screening test.

Factor	Low level	High level
Polymer dose, mg/l	1	5
Polymer type	PDADMAC	PAM
Rapid mixing intensity, rpm	200	400
Rapid mixing time, sec	0	60
Flocculation intensity, rpm	20	50
Flocculation time, min	5	15

The screening tests were repeated twice, the resulting significant factors, at a 5% level or below, are shown in Table 4.6. with respect to turbidity removal the test indicated that the initial SS concentration and JKL concentration was of great significance for both groups of polymers. The COD_f concentration was significant only for the low molecular weight polymers. The type of polymer was significant for the low molecular weight polymers. The molecular weight was significant for the high molecular weight polymers.

The test also indicated, that by manipulating mixing/flocculation parameters improvement of supernatant quality can be achieved. The rapid mixing intensity was not significant for both groups of polymers. However, the rapid mixing time was significant, especially for the low molecular weight polyelectrolytes. Flocculation time and intensity were significant for both groups.

The influence of several factors on turbidity removal became apparent in the screening test. In order to elucidate the effect of these factors the next step in the investigation was to perform Box Behnken design.

Box-Behnken design allows one to optimize one or several responses with respect to 3 to 6 design variables. The design may be rotated that ensures that each experiment contributes equally to the total information. As a consequence, the model will have the same precision in all directions from the centre.

Table 4.6. Results of screening tests.

Factor	**Effect on turbidity removal**	
	Low MW polymers	High MW polymers
SS concentration	+++	+++
COD_f	++	NS
Polymer dosage	+	+
pH	NS	NS
Temperature	NS	NS
Polymer type	++	NS
Molecular weight	NS	NS
JKL dosage	+++	+++
Rapid mixing intensity	NS	NS
Rapid mixing time	+++	++
Flocculation intensity	+	+
Flocculation time	NS	+

NS : no significant effect, P value ≥ 0,05
+ : significant effect, P value [0,01; 0,05]
++ : significant effect, P value [0,005; 0,01
+++ : significant effect, P value < 0,005

The experiments included three levels of each design variable: Low, Center, and High. Only continuous variables can be studied in Box-Behnken design, therefore separate designs were created for each polymer type. In the table Table 4.7 the factors investigated in the Box-Behnken design are listed. Although, two sets of experiments were designed, one excluded JKL, the other included JKL as the design variable.

for simplifying a dataset, by reducing multidimensional datasets to lower dimensions for analysis (Abdi, H.,2003).

Technically speaking, PCA is a linear transformation that transforms the data to a new coordinate system such that the greatest variance by any projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coordinate, and so on. PCA can be used for dimensionality reduction in a dataset while retaining those characteristics of the dataset that contribute most to its variance, by keeping lower-order principal components and ignoring higher-order ones. Such low-order components often contain the "most important" aspects of the data. But this is not necessarily the case, depending on the application.(Wikipedia, 2006).

Fig. 5.2 shows the PCA response plot. The model is based on the removal of turbidity, SS, total COD and COD$_f$. It is clear that the data are divided into two sub/sets (Group 1 and Group 2). The analysis of the data has indicated that such division is influenced by initial SS concentration. Group 1 includes samples with raw water SS concentration between 20 and 60 mg/l and Group 2 includes samples with SS concentration above 60 mg/l. The score plot indicates that the difference between Group 1 and Group 2 is too large to be described by the same model and therefore separate models should be created for each group. This means that the coagulation of diluted wastewater differs from coagulation of concentrated wastewater.

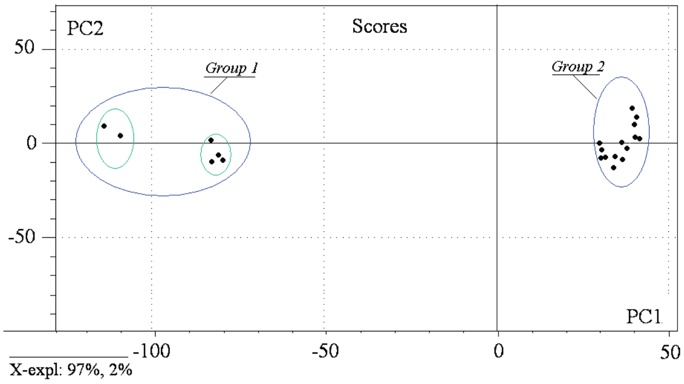


Fig. 5.2. PCA scores plot for wastewater coagulated by low molecular weight polyelectrolytes.

This difference can be seen from coagulation curves. It was observed that the shape of coagulation curves differ according to initial wastewater turbidity and suspended solids concentration. To illustrate this Fig. 5.3 is presented below.

Fig. 5.3 illustrates that the introduction of polyelectrolyte brought about some reduction of turbidity. The following increase of polyelectrolyte dosage cause an increase of residual turbidity and only at a quite high polyelectrolyte dosage a significant reduction of turbidity was observed. It can also be seen from Fig. 5.3 that the optimum specific dosage reduces with increasing of raw water turbidity.

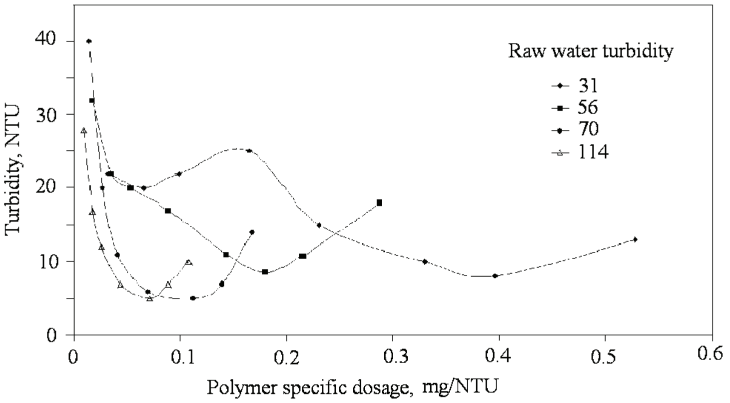


Fig. 5.3. Coagulation of municipal wastewater with low molecular weight polyelectrolyte ($PD_{800,100}$).

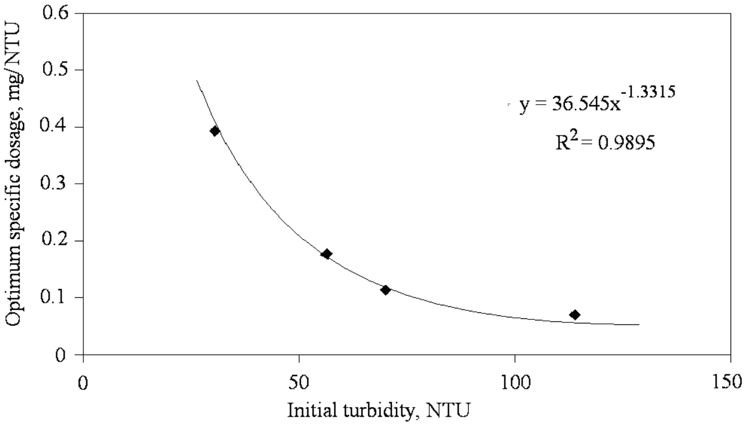


Fig. 5.4. Effect of initial wastewater turbidity on polyelectrolyte consumption, at a constant $COD_f = 56 mgO_2/l$.

Therefore, the optimum dosage was found to be strongly dependent on the initial turbidity. The demand for polyelectrolyte was lower for concentrated wastewaters than for diluted wastewaters. Fig. 5.4 below illustrates the effect of the initial turbidity on the polyelectrolyte consumption. Analysing data presented in Fig. 5.4 one can see that the optimum of specific dosage is dramatically reduced with increasing initial turbidity from 35 to 50 NTU.

A flocculation diagram based on experimental data for low molecular weight polyelectrolytes is presented in Fig. 5.5. The diagram was created using the coagulation curves. The lowest dosage of polyelectrolyte at which more than 50% of initial turbidity reduction has occurred was adopted as the beginning of flocculation. As the end of flocculation the lowest dosage at which an increase in turbidity was observed was adopted. The area inside the curve indicates the dosage range within which flocculation was observed. Analysing the Fig. 5.5 one can see that with the increasing of the initial turbidity, flocculation occurs over a broader range of the polymer dosages. At lower initial turbidity the flocculation was observed at higher dosage of polymer. Chaplain et al. (1995) reported the similar observation with a model suspension of silica and latex.

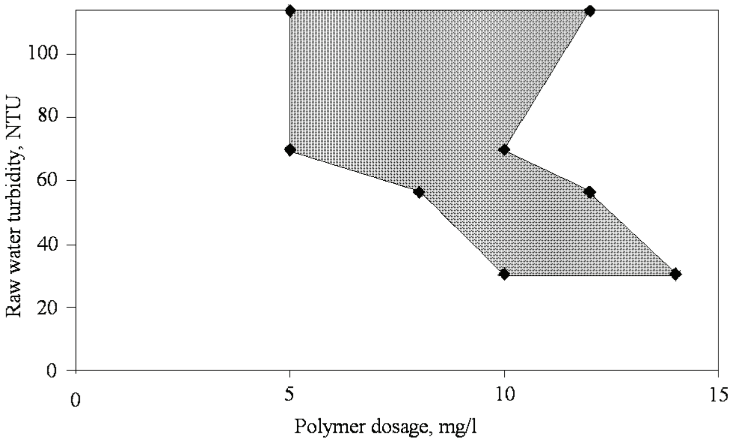


Fig. 5.5. Schematic phase diagram of the flocculation range of municipal wastewater by cationic polyelectrolyte ($PD_{800,100}$).

The effect of the suspended solids concentration on aggregation is shown in Fig. 5.6. The flocculation index changes within seconds after the dosing of polyelectrolyte. A rapid rise of flocculation index is followed by fall to a lower value. This behaviour is consistent with a rapid growth of the floc, followed by the break-up to smaller units. Monitor response rises during the flocculation step. At a very low energy input (10 rpm) the larger flocs begin to settle that is reflected in the monitor response as a decrease of the flocculation index.

In the wastewater with high initial concentration of the suspended solids (curves 3 and 4) the monitor showed changes in the aggregation state of the system immediately after dosing the polymer. The rate of rise of the flocculation index is steeper and no lag time was observed even at low polymer dose in contrast to the wastewater with low solids content (curves 1 and 2).

As the number of the particle-polymer collisions occurring in unit volume per unit time (or flocculation rate), J_{ij} is given by:

$$J_{ij}=k_{ij}N_iN_{j,,} \qquad \text{eq. 5-1}$$

where N_i and N_j are, respectively, the initial number of the particles and the polymer molecules per unit volume and k_{ij} is the rate constant.

Therefore, a higher flocculation rate observed in concentrated wastewaters is explained by eq. 5-1.

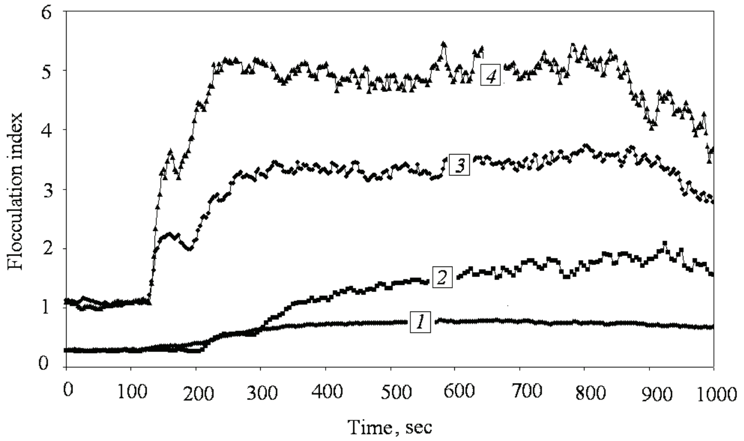


Fig. 5.6. Influence of initial suspended solids concentration on flocculation index, (1) – 3 mg/l, SS_{in}- 130mg/l, (2) – 5 mg/l, SS_{in}- 130mg/l, (3) – 3 mg/l, SS_{in}- 580mg/l, (4) – 5mg/l, SS_{in}- 580mg/l.

The increase of the suspended solids concentration leads not only to the higher flocculation rate, but to the formation of bigger floc as well. This was observed as an increase of the plateau value of the flocculation index. Fig. 5.7 shows how the concentration of the suspended solids in the influent affects the floc size.

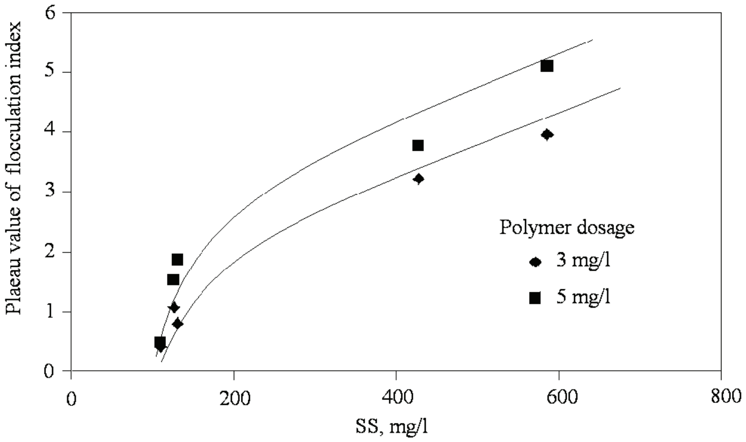


Fig. 5.7. Influence of suspended solids concentration on floc size.

Fig. 5.8 illustrates the effect of the initial wastewater turbidity on the residual turbidity at the optimum polyelectrolyte dosage. The tendency is clear: an increase of the initial

Fig. 5.11 shows the effect of organic matter concentration on optimum polyelectrolyte dosage.

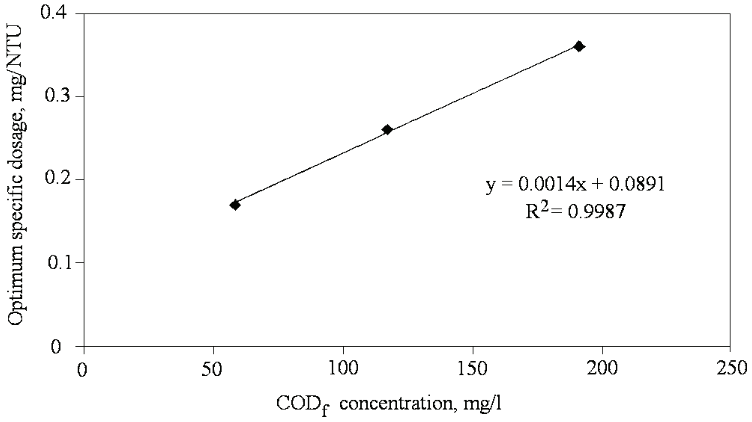


Fig. 5.11. Effect of organic matter concentration on optimum polyelectrolyte dosage.

5.3 Effect of polyelectrolyte properties on coagulation-flocculation

The coagulation with polyelectrolytes as primary coagulants follows the classical pattern, as the dosage of polyelectrolyte increases the quality of supernatant improves until the maximum at the optimal dosage is reached. The subsequent addition of polymer leads to overdosing and restabilisation of suspension, observed as an increase in the residual turbidity.

The optimum dosages vary from polymer to polymer. Generally, optimum dosage is slightly lower with PDADMACs than with P-Epi-DMAs. A relatively narrow destabilisation region is found in both of the groups of low molecular weight polymers. The high molecular weight polymers were characterised by broader destabilisation region.

With respect to maximum turbidity and SS removal, the optimal coagulant dose was similar for PDADMACs and PAM while P-Epi-DMAs exhibited a maximum removal rate at dosages 30-50% higher than those of PDADMACs of similar molecular weight. The optimum dosages for PDADMACs and PAMs were 10mg/l or less, giving on the average 75% removal of turbidity and 80% removal of SS. P-Epi-DMAs were inferior to PDADMACs and PAMs at the same dosage, but giving the same removal at dosages of 15mg/l or higher.

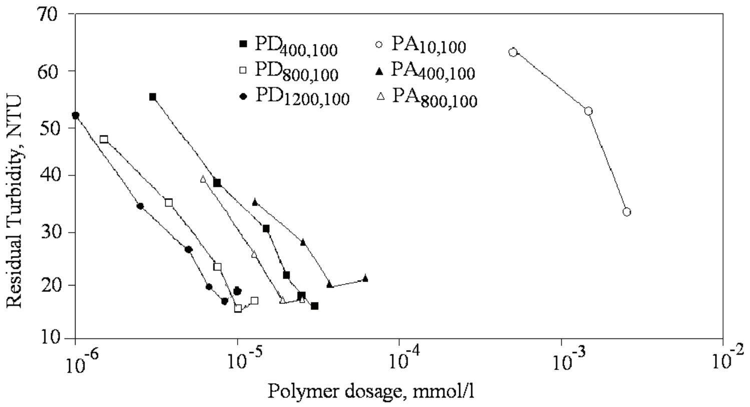


Fig. 5.12. Residual turbidity as a function of polymer dosage.

Regardless of polymer type, molecular weight of polyelectrolyte has affected removal efficiency. A considerably broader destabilisation region, compare to the low molecular weight ones, characterised the coagulation with high molecular weight polymers. The optimum dosage was affected by initial wastewater turbidity (SS). At the optimum dosage 80% of turbidity and SS were removed.

Fig. 5.13 illustrates how the dosage necessary to remove a certain amount of SS changes with the MW of polyelectrolyte. Presented in logarithmic-scale the relationship between polymer MW and dosage is linear. Both PDADMACs and P-Epi-DMAs show the similar trend towards a dosage decreasing with a MW increasing. Nevertheless, there is a difference between two groups of polymers. While for PDADMACs the effect of molecular weight on dosage is quite considerable, for P-Epi-DMAs the same effect is moderate.

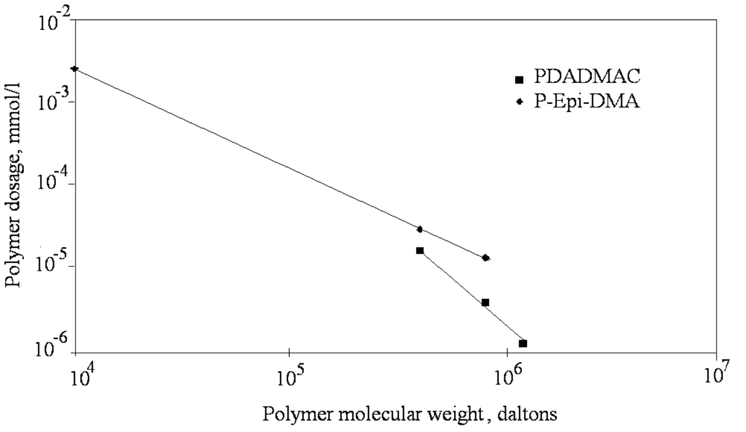


Fig. 5.13. The dosage of polyelectrolyte necessary to remove 50% of SS as function of MW.

All polymers performed nearly the same with respect to Turbidity and SS removal, except for $PA_{10,100}$ that exhibited very poor particle removal efficiency. The polymer $PA_{10,100}$ clearly illustrates the effect of molecular weight, or rather amount of charge introduced into the system. Since $PA_{10,100}$ is a homopolymer, containing charged group in every monomer unit, the number of elementary charges in molecule is strongly associated with molecular weight. A very low molecular weight of this polymer leads to its inability to form "bridges" and promote aggregation of destabilised particles.

The experimental data indicate that the dosage of P-Epi-DMA of a certain molecular weight is some how higher than the dosage of its PDADMAC analogue. Taking into consideration the fact that P-Epi-DMAs have a higher charge density, one may conclude that the factors other than amount of charge control the coagulation process. The structure of PDADMAC molecule suggests that the observed phenomenon be due to hydrophobicity of PDADMAC. PDADMAC posses a large hydrophobic part and therefore the hydrophobic interactions might be involved in destabilisation process. The nature of hydrophobic interactions was discussed in chapter 2.

5.4 Effect of polyelectrolyte properties on colloids destabilisation

The primary purpose of this set of experiments was to study the stability of colloidal particle as affected by the polyelectrolyte molecular weight, the polyelectrolyte type and the concentration of the soluble organic matter.

It was expected that the particle stability would be primarily dependent on the amount of the charge introduced. In order to investigate the role of the polyelectrolyte charge in the destabilisation process, the polyelectrolytes with different charge densities and different molecular weight were used.

The zeta-potential was measured in the wastewater before and after coagulant addition. Fig. 5-14 and Fig. 5-15 illustrate the effect of the polymer dosage on the particle stability. The adsorption of the macromolecule on the particle surface entails the charge neutralisation and reduction of the zeta-potential of colloidal particles. With increasing polymer dosage gradual reduction of the zeta-potential to 0 was observed. The pattern of the destabilisation curve was clearly dependent on the polyelectrolyte characteristics. The common for all polyelectrolytes was that the zero value of the zeta-potential was observed at dosages lower than the optimum flocculation concentration.

In both instances the increase of the molecular weight leads to the particle destabilisation at lower dosage. This is especially pronounced with the polyamines (Fig. 5-14), since the difference in the molecular weight is more considerable. The polyelectrolytes (P-Epi-DMA and PDADMACs) involved in this experiment are 100% charged. Therefore, approximately 40 times more polyelectrolyte with lower molecular weight ($PA_{10,100}$) has to be adsorbed, compare to the higher molecular weight analogue ($PA_{800,\ 100}$) in order to introduce the same amount of charge.

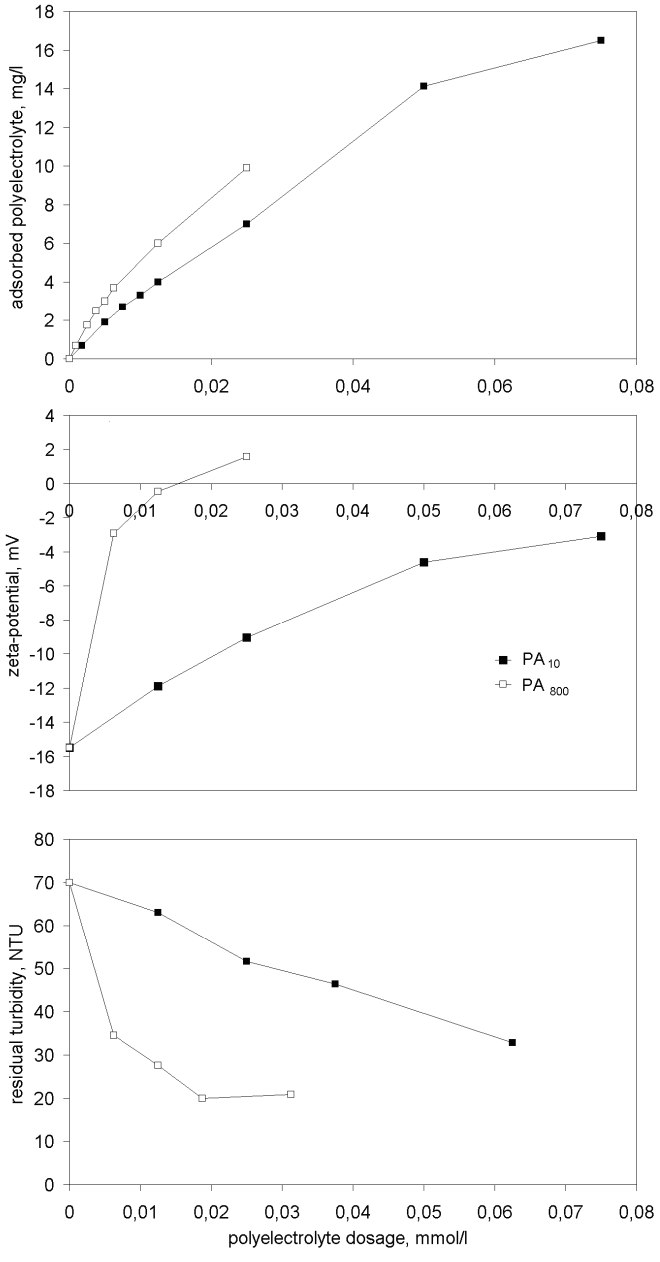


Fig. 5-14. Effect of polymer dosage on particle stability when coagulating wastewater by P-Epi-DMAs ($PA_{10,100}$, $PA_{800,100}$).

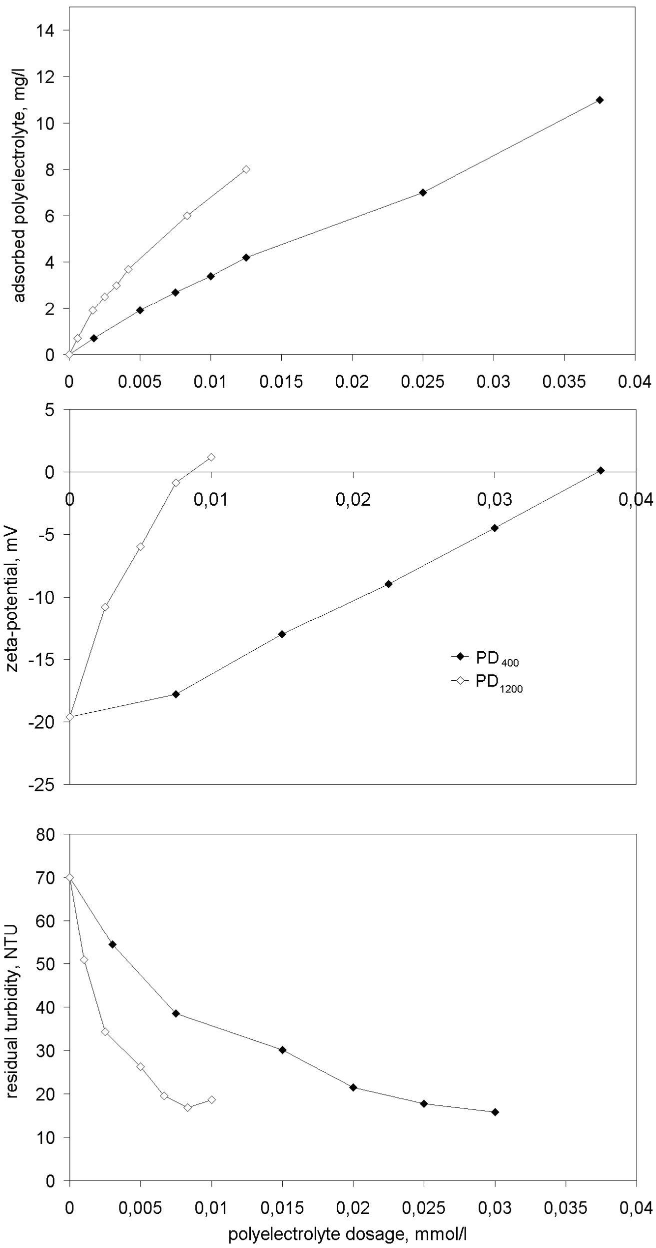


Fig. 5-15. Effect of polymer dosage on particle stability when coagulating wastewater by PDADMACs ($PD_{400,100}$, $PD_{1\,200,100}$).

The adsorption data in Fig. 5-14 and Fig. 5-15 clearly indicate that at the zero zeta-potential the system is far from saturation with polyelectrolyte. This may be due to the presence of another consumer of the polyelectrolyte aside of the colloidal and suspended particles.

Fig. 5-16 and Fig. 5-17 illustrate the effect of the soluble organics on coagulation with polyelectrolytes. In wastewater with low concentration of soluble organics the zero potential is reached at considerably lower dosage. Besides, the effect of the polyelectrolyte charge density is seen. The P-Epi-DMA based polymer has a higher charge density than the PDADMAC of the same molecular weight. From Fig. 5-16 can be seen that at the same dosage the P-Epi-DMA brings about greater reduction of the zeta-potential.

The introduction of the additional amount of the soluble organics reduces initial zeta-potential of the particles (Fig. 5-17). That is a result of adsorption of the organic molecules on the particle surface. At the same time the stability of the particles become greater and the higher dosages of the polyelectrolytes were necessary to reduce the zeta-potential to near zero.

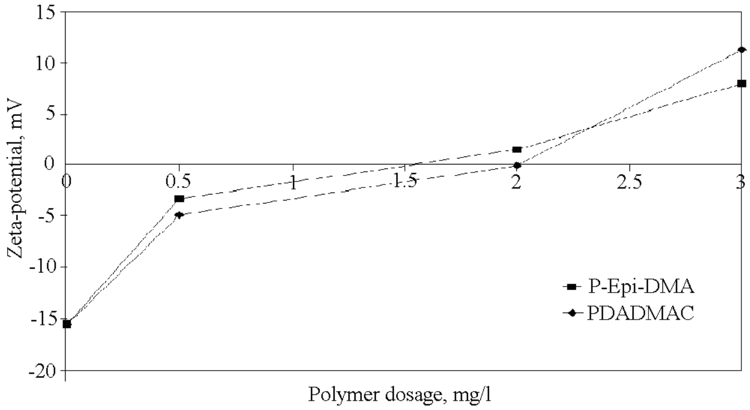


Fig. 5-16. Reduction of zeta-potential in wastewater with low concentration of soluble organics, coagulated by polyelectrolytes.

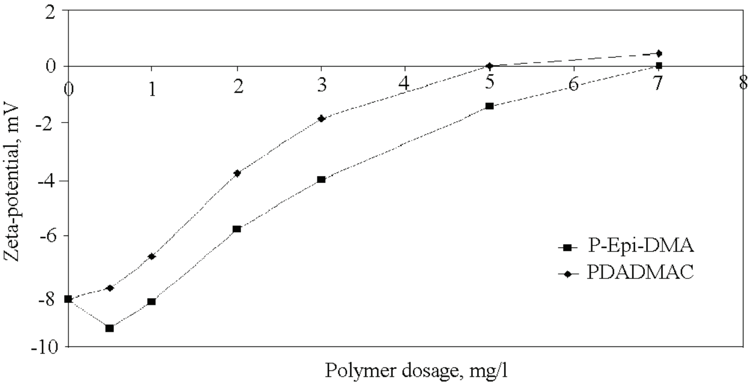


Fig. 5-17. Reduction of zeta potential in wastewater with high concentration of soluble organics, coagulated by polyelectrolytes.

5.5 Effect of polyelectrolyte properties and dosage on aggregation

No effect of polyelectrolyte molecular weight or polyelectrolyte type on aggregation kinetic or floc size was observed. The effect of the polyelectrolyte dosage on aggregation was similar for both PDADMACs and P-Epi-DMAs. Both the value of the flocculation index and the rate of increase of the flocculation index were affected by the polyelectrolyte dosage.

The flocculation results for the various dosages of PDADMAC ($PD_{800,100}$) are illustrated in Fig. 5-18. The curves show characteristic features. With increasing polymer dosage the rate of rise in flocculation index becomes steeper. Depending on the polymer dose not only the slope but also a general shape of the flocculation curve varies. At low dosage of the polymer (curves 1 and 2), after the polyelectrolyte addition the flocculation index rises by approximately 10% and then does not change for some time (lag time).

With increasing of the polymer dosage the lag time disappears, and the slope rate significantly increases (as for curves 3 and 4 in Fig. 5-19). The slope provides an empirical measure of the “flocculation rate”. The existence of this lag time at a low polyelectrolyte dosage can be explained by the theory of polymer adsorption.

According to the theory, the maximum adsorption rate corresponds to 50% of the surface coverage. In order to achieve particle destabilisation sufficient for flocculation to occur a significant fraction of the added polymer needs to be adsorbed. At low polymer dose this fraction may be as high as 90% of the initially added polymer, while at doses close to the optimum and higher this fraction may be less than 20%. So, when the dose of polymer increases, the aggregation begins immediately after the polymer addition (shown by arrow). Immediately after the polyelectrolyte addition some increase of FI was observed.

Later in this chapter will be demonstrated that the polyelectrolyte interacting with the soluble organics forms the precipitate. The formation of the precipitate increases concentration of the particles in the system. This fact leads to increase of FI, which can be seen from Fig. 5-18 (curves 1 and 2).

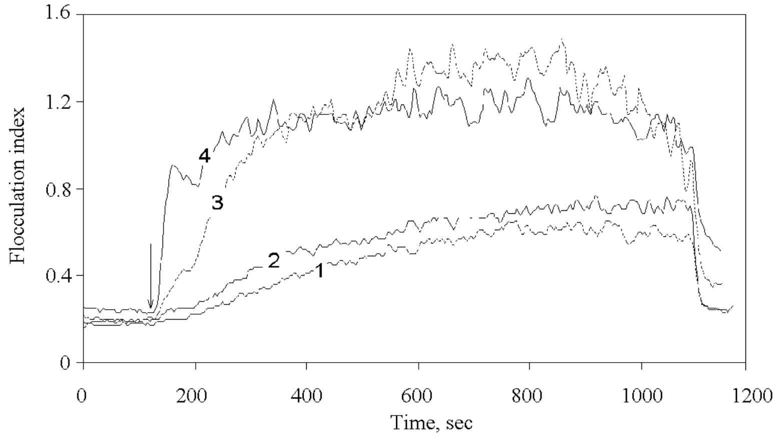


Fig. 5-18. Effect of polyelectrolyte dosage ($PD_{800,100}$) on particles aggregation (curve (1) – 3mg/l, (2) – 5mg/l, (3) – 7mg/l, (4) – 11mg/l).

The plateau value of FI increases with increasing of the dosage up to a certain degree, after further dosage increase the plateau value decreases. In Fig. 5-19 the plateau value and the greatest rate of increase in flocculation index are plotted against the coagulant dosage.

The value of the maximum flocculation index (the plateau value) is an empirical characteristic of the floc size. As seen from Fig. 5-19, the maximum plateau value was observed at a polymer dosage 7mg/l. For the model suspensions the plateau value correlates very well with the turbidity of the treated water (Gregory, 1989). In tests with real wastewater the maximum plateau value was observed at the dosages lower than the optimum flocculation concentration. For the data presented in Fig. 5-19 the optimum flocculation concentration was 11mg/l, while the maximum plateau value was observed at 7mg/l.

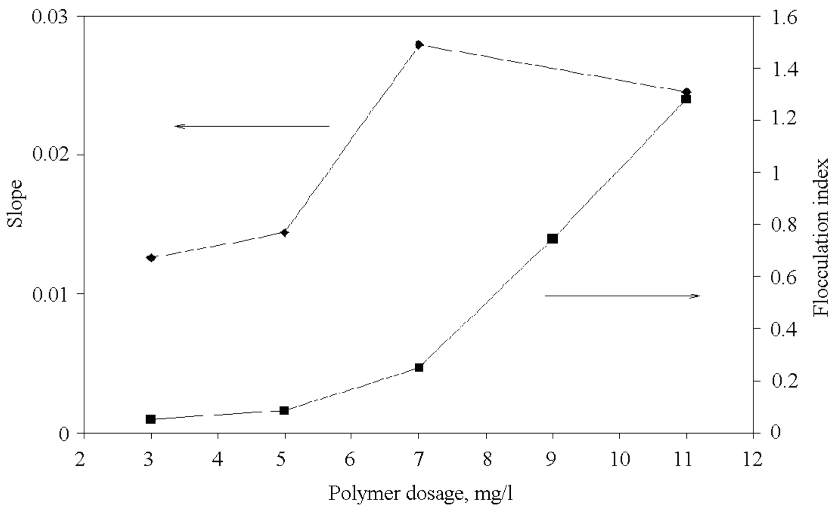


Fig. 5-19. The influence of polymer dose on flocculation index and flocculation rate.

The flocculation experiments followed by the floc destruction and reflocculation were performed, the flocculation curves obtained are presented in Fig. 5-20. Arrows point the polymer addition, application of the high shear rate and beginning of the reflocculation. For the floc destruction 400 rpm was applied for 1 minute, the following reflocculation was identical to those applied in all experiments: 50 rpm for 5 min, 30 rpm for 5 min and 10 rpm for 5 min.

As seen from the figure, even at low polyelectrolyte dosages the floc is not destroyed completely after applying the high share rate. The flocculation index is larger than the initial flocculation index. This indicates that some irreversible changes have occurred in the system.

With increasing polyelectrolyte dosage the magnitude of these changes increases. The degree of the floc reconformation decreases with increasing polyelectrolyte dosage. At polymer dose 3mg/l the floc produced after the second flocculation procedure has practically identical size to those produced during the first flocculation step. With increasing polymer dose the degree of reconformation decreases, thus at dose 11mg/l the size of the floc after the second flocculation step is about 75% of the floc obtained during the first flocculation.

The increase of the flocculation index after the floc destruction, compare to initial flocculation is a consequence of the increased amount of particles in the system. The data obtained during these experiments correspond to the data described in section 5.7.2of this chapter. Therefore, one can speculate that the formation of the additional amount of solids occurs due to polymer interaction with soluble organics. With increasing polyelectrolyte dosage more insoluble complexes are produced. It leads to increase of the flocculation index.

The microscopic images of the floc produced at different dose of the polyelectrolyte indicate that at lower doses the floc is denser, the distance between the primary particles in aggregates is smaller and the polymer does not form a network. The pictures of the floc are presented in Fig. 5-21.

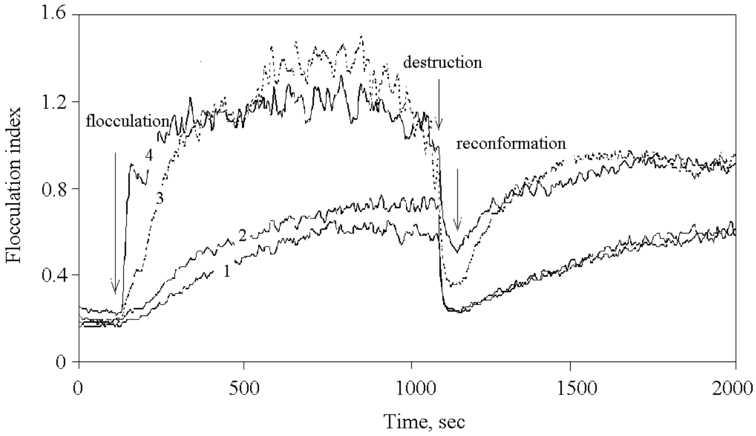
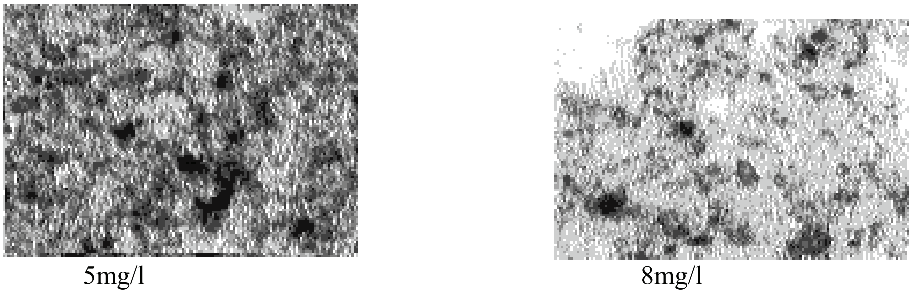


Fig. 5-20. Floc destruction and reconformation (curve (1) – 3mg/l, (2) – 5mg/l, (3) – 7mg/l, (4) – 11mg/l).


5mg/l

8mg/l

Fig. 5-21. Floc structures at different dose of polyelectrolyte (x100).

5.6 Dual coagulant. Influence of low dosage of inorganic coagulant on coagulation flocculation with polymers

Combination of inorganic coagulant with polyelectrolytes is widely used in water and wastewater treatment to enhance the primary treatment. In the most cases large dosages of iron or aluminium salts are followed by anionic polyelectrolyte. In the experiments a different scheme was tested: the dosage of iron far insufficient to destabilise wastewater particles was followed by cationic polyelectrolyte. Below results of coagulation of municipal wastewater by polyelectrolytes combined with a low dosage of iron salt are presented and discussed.

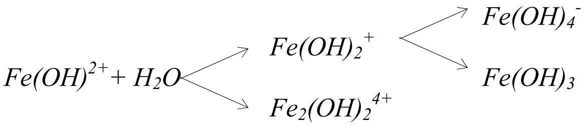
A combination of inorganic salt and different cationic polyelectrolytes was tested for the municipal wastewater treatment. First inorganic coagulant was added to the wastewater at a dosage of 0.1 or 0.2mmol/l, followed by the rapid mixing (400 rpm) for 20 sec and then polyelectrolyte was applied at dosages of 1 to 4mg/l. The suspension was flocculated, allowed to settle and the supernatant was analysed for turbidity, SS, COD and ortho-phosphates.

5.6.1 Mechanism

As an inorganic coagulant the product called JKL was used in this research. JKL is a commercial name for $FeClSO_4$. Since the salt is formed by the weak base and the strong acid, it undergoes hydrolysis when solutes in water. The interaction of $FeClSO_4$ with water is described by following reactions:

$$FeClSO_4 + H_2O \rightarrow Fe^{3+} + Cl^{-} + SO_4^{2-}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+}$$



$$Fe(OH)^{2+} + H_2O \rightarrow \begin{cases} Fe(OH)_2^{+} \rightarrow \begin{cases} Fe(OH)_4^{-} \\ Fe(OH)_3 \end{cases} \\ Fe_2(OH)_2^{4+} \end{cases}$$

At pH around 7, according to the diagram presented in Fig. 5.22, $Fe(OH)_4^{-}$, $Fe(OH)_2^{+}$, $Fe(OH)^{2+}$ and $Fe(OH)_3$ are presented at the equilibrium. Since in wastewater there is enough alkalinity to form hydroxide, the major component of the system is a precipitate of $Fe(OH)_3$.

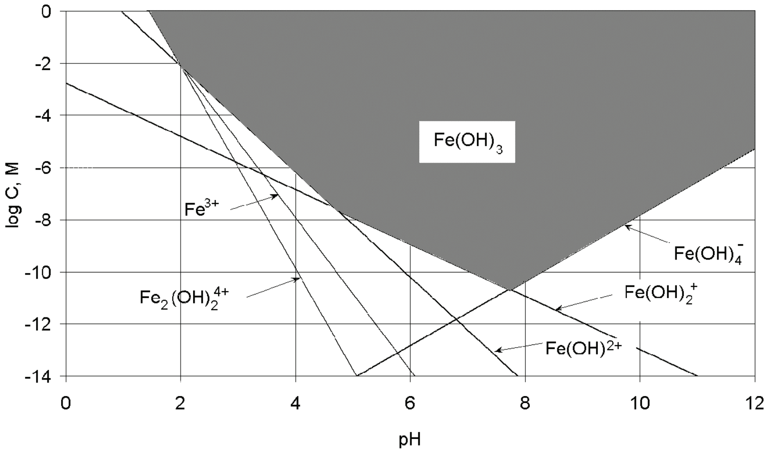


Fig. 5.22. Equilibrium composition of solution in contact with freshly precipitated $Fe(OH)_3$ (From Stumm and O'Melia, 1986).

The formation of the precipitate ($Fe(OH)_3$) increases concentration of the particles in the system. It was observed as an increase of the flocculation index immediately after addition of JKL. But the effect of JKL is far beyond the effect of the only increased particle concentration. The anions Cl^- and especially SO_4^{2-} suppress the charge of the polyelectrolyte, so that the polyelectrolyte molecules can interact with each other. In addition, the hydrophobic force can contribute. All these factors lead to the increase of the floc size as illustrated by Fig. 5.23. The dose of JKL used was 0.1mmol/l (or 5,6mg/l) Fe^{3+} followed by 1mg/l of polyelectrolyte. As is seen from the figure, addition of a small amount of the inorganic coagulant significantly increases both the flocculation index and the rate of increase of the flocculation index.

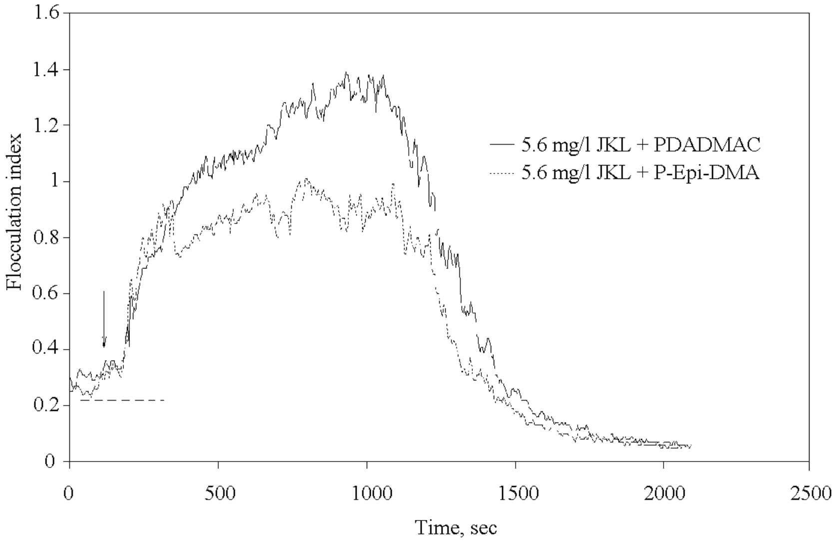


Fig. 5.23. Monitoring of floc produced by combined inorganic salt-polymer coagulants.

5.6.2 Performance

Fig. 5.24 and Fig. 5.25 illustrate the effect of inorganic coagulant on the turbidity removal efficiency.

An introduction of the inorganic coagulant resulted in a significant improvement of the supernatant quality. As low dosage of JKL as 0.1mmol (Fe^{3+})/l, combined with 1mg/l of poly-amine based polymer F, increased the turbidity removal efficiency from 10% to 55%. The combination of 0.1mmol/l of JKL with high molecular weight polyelectrolyte (Fig. 5.25) improve treatment efficiency by 30%. The higher dosage of JKL (0,2mmol(Fe^{3+})/l) provides even better turbidity removal.

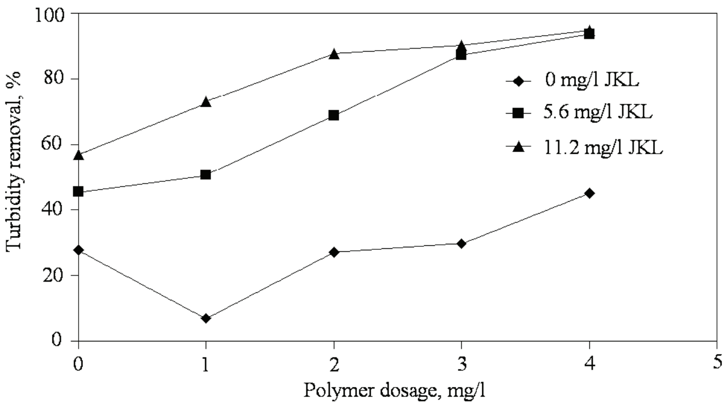


Fig. 5.24. Low molecular weight polymer ($PA_{800,\ 100}$) combined with low dosage of Fe(III) salt.

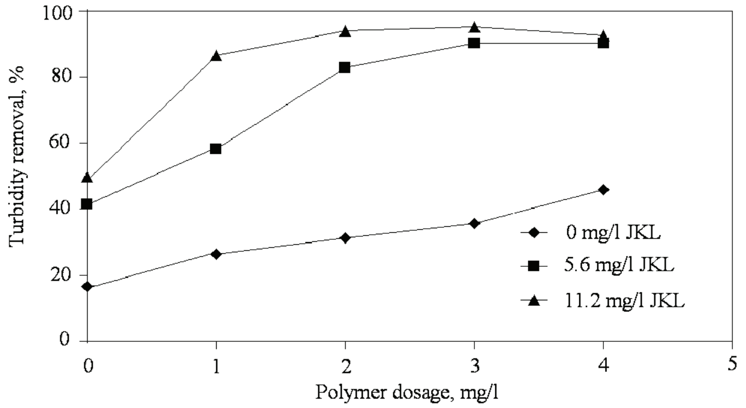


Fig. 5.25. High molecular weight poly-akrylamide ($PM_{10000,40}$) combined with low dosage of Fe(III) salt.

Table 5.1 gives the overview over the treatment results obtained when the dual coagulant was used. As seen from the data, the dual coagulants were very effective for both colloidal and organic matter removal. All tested polyelectrolytes performed nearly the same, giving residual Turbidity and SS under 10 NTU and 15mg/l, respectively.

Table 5.1. Turbidity and SS removal when coagulating municipal wastewater by cationic polyelectrolytes combined with JKL.

Polymer	**Polymer dose (mg/l)**		**Removal (%)**			
			Turbidity		**SS**	
	JKL 0.1 mmol/l	JKL 0.2 mmol/l	JKL 0.1 mmol/l	JKL 0.2 mmol/l	JKL 0.1 mmol/l	JKL 0.2 mmol/l
$PD_{400,100}$	3	2	94	96	94	95
$PD_{800,100}$	2	3	94	95	95	97
$PD_{1200,100}$	1	1	95	96	96	97
$PA_{10,100}$	3	2	75	80	80	87
$PA_{400,100}$	3	3	89	90	92	93
$PA_{800,100}$	3	2	88	90	89	92
$PM_{10000,40}$	4	3	93	94	97	97
$PM_{10000,70}$	4	3	94	95	97	97

5.6.3 Sludge production

The sludge produced in the physical-chemical treatment is mainly due to the amounts of the organic matter and the total solids in suspension that are removed. Some additional sludge can be formed as the result of the interaction between coagulant and water. Therefore, the amount of sludge produced depends on the type of coagulant used, dosage applied and the operating conditions. Inorganic coagulants are known to produce an additional sludge as a result of the metallic hydroxide precipitation. Organic coagulants do not produce insoluble hydroxides, but as was shown above they form precipitate trough the interaction with dissolved organic matter. Both this reactions will influence the amount of sludge produced.

The precipitation of the metallic hydroxide occurs simultaneously with the use of the inorganic coagulant. The dispensed coagulant is dissociated and ionised into metals that instantly precipitate as hydroxides if the water has the required alkalinity.

$$2FeClSO_4 + 3Ca(HCO_3)_2 + 6H_2O \rightarrow 2Fe(OH)_3 + 2CaSO_4 + CaCl_2 + 6H_2CO_3 \qquad eq.\ 5\text{-}1$$

Therefore, according to the stoichiometric ratio, every gram-molecule of *$FeClSO_4$* produce 1 gram-molecule (or 107 g) of metallic hydroxide. The total amount of the sludge produced consists of the suspended solids removed, the sludge formed by precipitated metallic hydroxide and the sludge formed by the removed colloidal and dissolved organic matter:

$$SP = SS\ removed + Fe(OH)_3 + SS_{<1\mu m}\ removed \qquad eq.\ 5\text{-}2$$

The production of sludge has been determined and expressed as the amount of sludge (mg) per *l* of water treated. In order to compare the results obtained with each coagulant, the ratio between the amount of sludge produced and the amount of COD and SS removed has been estimated by taking into account the performance of the removal of the organic and the suspended matter.

Fig. 5.26 illustrates the effect of inorganic coagulant dosage on the SP/SS removal index. It is seen from the data that the rate of increase depends on the initial SS concentration in wastewater.

Fig. 5.27 illustrates the sludge production as affected by dosage of the inorganic coagulant. As the dosage of Fe^{3+} increases the sludge production increases due to larger amount of $Fe(OH)_3$ produced. The application of the polyelectrolyte after the iron salt causes a reduction of sludge production/suspended solids removed ratio. This is due to significant improvement of SS removal and increase of the denominator while keeping the numerator almost unchanged.

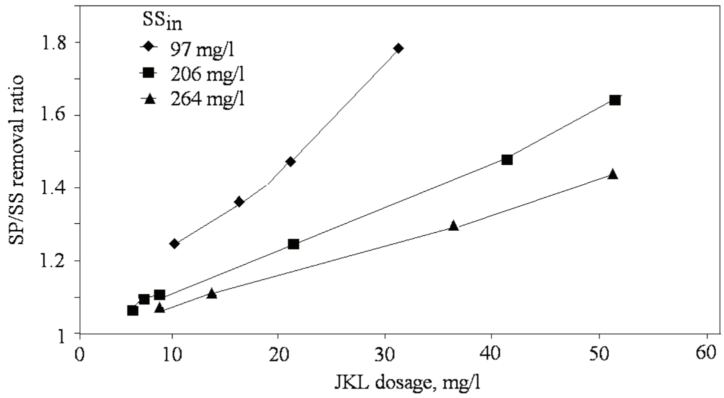


Fig. 5.26. Sludge production as a function of JKL dosage and suspended solids in raw wastewater.

If there is no coagulant applied the SP/SS removal index is equal to one. If polyelectrolyte is applied as the only coagulant, the SP/SS removal index is not equal to one. The SP/SS removal index increases as a result of removal of colloidal particles and dissolved matter, as was discussed above. Depending on the polyelectrolyte type from 10 to 25% more sludge was produced in the experiments, as a result of colloidal and soluble matter removal.

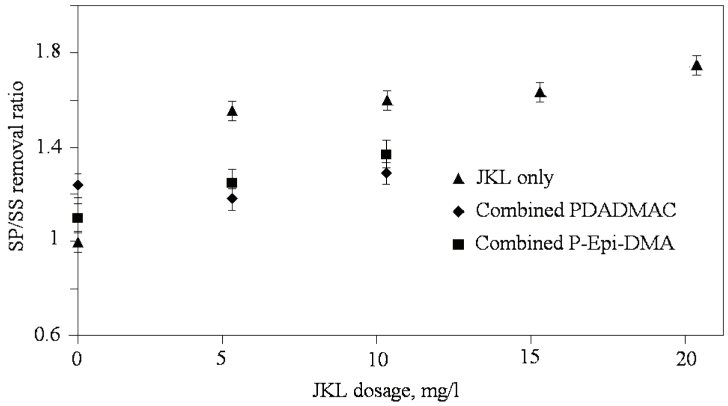


Fig. 5.27. Sludge production as a function of inorganic coagulant dosage.

Fig. 5.28 shows that the PDADMACs produced the least amount of sludge for a given amount of COD removed both when used alone and when combined with JKL. The production of sludge in the case of P-Epi-DMAs was very similar. Both PDADMACs and P-Epi-DMAs removed a large amount of the soluble organic that combined with a good removal of the particulate COD that gave a sludge production/ COD removal ratio about one. The PAMs produce the greatest amount of sludge per mg COD removed.

This is due to the much lower COD_f removal compare to those of PDADMACs and P-Epi-DMAs.

Introducing JKL the precipitation of the metal hydroxide takes place. As a result more sludge is produced (it was discussed above). On the other hand, the JKL/polymer combined coagulant promotes the particulate and COD_f removal that compensates the increase in sludge production. The balance between these two processes predetermines the effect of JKL on the sludge production/COD removal ratio.

Fig. 5.28 illustrates that the effect of JKL dosage on the sludge production/COD removal ratio depends on the polymer type. The observed reduction of the sludge production/ COD removal ratio with increasing dose of JKL in combination with the P-Epi-DMAs and PAMs may indicate a synergetic effect of these combinations on COD removal compare to the JKL/PDADMAC combination.

Fig. 5.29 shows the ratio between the production of sludge and the amount of suspended matter removed. Since the polyelectrolytes do not produce additional sludge in form of the hydroxide precipitate, the sludge production/SS removal ratio was expected to be around 1. The higher values obtained for the PDADMACs and the P-Epi-DMAs are due to removal of the colloidal matter (<1μm) and precipitation of the soluble organics. The PAM based polymers as solo coagulant produced the least amount of sludge, due to their inability to remove the soluble organics. Combined with JKL, the PDADMACs produced the least amount of sludge that corresponds to a SP/TSS removed ratio of around 1.2.

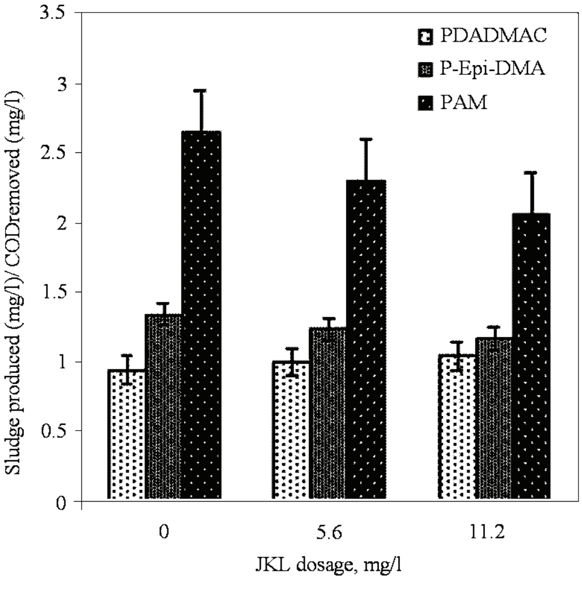


Fig. 5.28. Ratio between the amount of sludge produced (mg/l) and the COD (mg O_2/l) reduced for different polymers as a function of JKL dose.

The treatment and handling of the sludge generated in the coagulation-flocculation process are important aspects to consider when choosing the products to be used as coagulants. Considering the results obtained, the most suitable solo coagulants would be the PAM based polyelectrolytes if the removal of the soluble organics is not an issue and if a low sludge production is a major goal. Considering both particle removal and organic matter removal, the most suitable solo coagulant would be the PDADMAC based product. When also phosphate has to be removed, a combined coagulant should be used and in this case. The combination giving least amount of sludge seems to be JKL/PDADMACs.

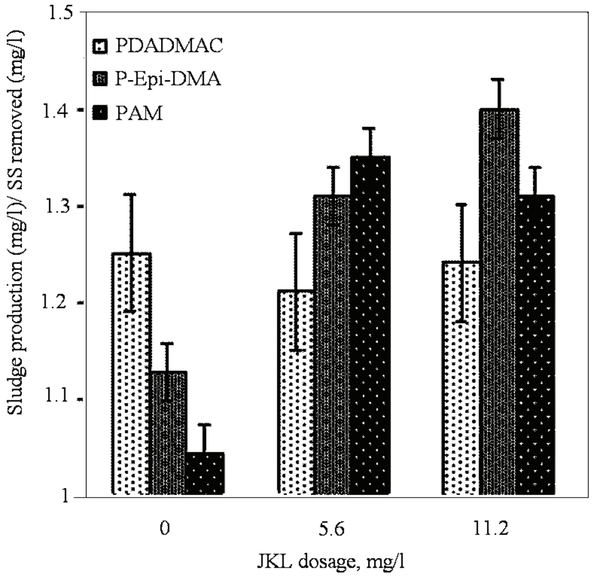


Fig. 5.29. Ratio between the amount of sludge produced (mg/l) and the SS (mg/l) removed for different polymers as a function of JKL dose.

5.6.4 Removal of phosphates

The removal of phosphates is not among the goals when the polyelectrolytes are used as primary coagulants. However, based on the chemical structure of cationic polyelectrolytes, some removal of the ortho-phosphates can occur.

As was described before, the cationic polyelectrolytes are poly-ionic compounds formed by the poly-cation and the chloride anion. The ion exchange reaction can take place if solubility of the poly-cation phosphate complex is lower than the solubility of the poly-cation chloride complex. Since in wastewater the number of compounds competing for the cationic group of the polyelectrolyte is large and most of them form stronger bound with the cationic group, the removal of the ortho-phosphates can not be considerable.

The molybdenum blue spectrophotometric method is adopted in Norway as a standard method for orthophosphate determination in water and wastewater (Norsk Standard NS4724, 1984). The method is based on the production of molybdophosphoric acid that is reduced to intensively coloured molybdenum blue by the ascorbic acid. The determination of the residual orthophosphates in wastewater treated with the polyelectrolytes is complicated. Problems are caused by interaction of the residual polyelectrolyte with the molybdate anion, which is the main reagent in phosphate determination.

The interference effects of the poly-diallyl-N,N-dimethylammonium chloride (PDADMAC) and the poly-2-hydroxypropyl-N,N-dimethylammonium chloride (P-Epi-DMA) on the phosphate determination by the molybdenum blue method is not straight forward. Both polyelectrolytes exhibit the similar trend, and at concentration lower than 2mg/l suppress the blue tint formation by reducing the strength of absorption at a wavelength of 880nm. At the concentration of the polyelectrolyte >2mgl^{-1} the hypochromic effect disappears and absorbance increases with increasing polyelectrolyte concentration. At the polyelectrolyte concentrations > 10mgl^{-1} misleading results were obtained due to increased turbidity of the analysed mixture. The interference effect from polyelectrolytes is due to interaction between cationic group of polyelectrolytes and molybdate anion that results in production of white-blue flakes of sediment. At nonstoichiometric concentrations the complexes produced are soluble. Therefore, at lower polyelectrolyte concentrations the interfering effect is probably due to consumption of molybdate ions preventing them from interaction with phosphate. At high concentration of polyelectrolyte interference is a consequence of increasing turbidity. The interference might be quite significant when analysing orthophosphate in waters treated with polyelectrolyte, since the levels of residual polyelectrolyte vary between 0.15 and 10 mgl^{-1} (Becker *et al.,* 2000)

Therefore, even the removal of orthophosphates was observed in the experiments, the data for phosphate removal is not reported here due to uncertainty of the degree of interference caused by the residual polyelectrolyte.

Fig. 5.30 illustrates the phosphorous removal by the dual coagulant (low dosage JKL combined with high molecular weight polyelectrolyte). The dual coagulants demonstrated good ortho-phosphate removal efficiency. More than 80% of ortho-phosphates were removed applying only 0.1mmol/l of Fe^{3+} and 2mg/l polyelectrolyte. The initial concentration of the ortho-P in the wastewater varied from 0.42mg/l (or 0.005mmol/) to 1,14mg/l (or 0,014mmol/l). Therefore the excess of Fe^{3+} (according to the stoichiometric ratio of precipitation reaction) varied between 20 and 7 times.

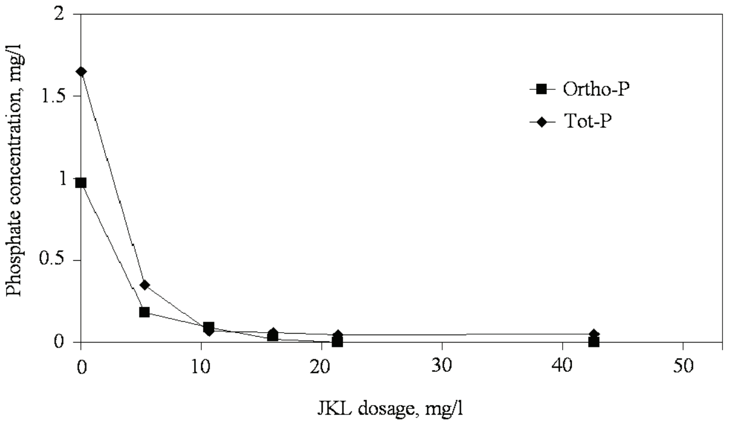


Fig. 5.30. Phosphorous removal by dual coagulant, polymer dosage: 2 mg/l.

5.7 Mechanism of polyelectrolyte interaction with wastewater

The complexity of wastewater as a coagulation flocculation system makes it very difficult to investigate and identify the predominant mechanism. Anyway some specific aspects are worthwhile to discuss, such are effect of particle size on the removal efficiency and interaction between polyelectrolyte and soluble organic matter.

5.7.1 Particle size distribution

During coagulation-flocculation not only the concentration of the particles reduces, but the particle size distribution changes as well.
Fig. 5.31 illustrates the change of the particle size distribution during coagulation-flocculation. The particle size distribution was measured after the flocculation step in order to keep the solids concentration relatively constant.

It is seen from Fig. 5.31 that the volume of two particle fractions changes significantly during coagulation-flocculation. The volume of the particles bigger than approximately 40µm significantly reduces after the polymer addition and flocculation. This reduction is a result of destruction of the initially presented large aggregates during the rapid mixing. When the higher polymer dosage is applied the volume fraction of the particles bigger than 20µm increases again. That corresponds to the data obtained during flocculation monitoring with PDA instrument.

The volume of the particles smaller than ≈40µm reduces with increasing polymer dosage. At the optimum dosage the volume of this fraction is one third of the initial volume.

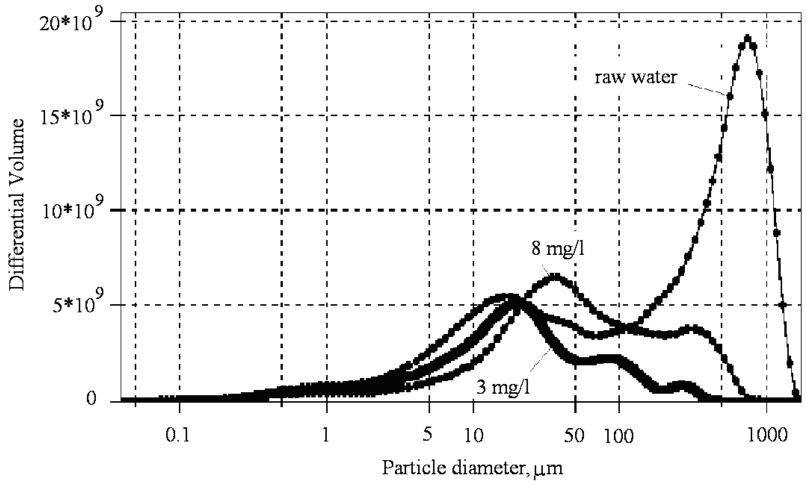


Fig. 5.31. The change of particle size distribution during coagulation-flocculation of wastewater by polyelectrolytes.

Fig. 5.32 gives better insight into the changes occurring within the fraction of particles smaller than 1μm. The curves clearly indicate that during coagulation-flocculation the number of the particles bigger than 0.3μm decreases. At the same time the number of the particles smaller than 0.3μm increases. This increase is probably due to the formation of complexes between the polyelectrolyte and the soluble organics.

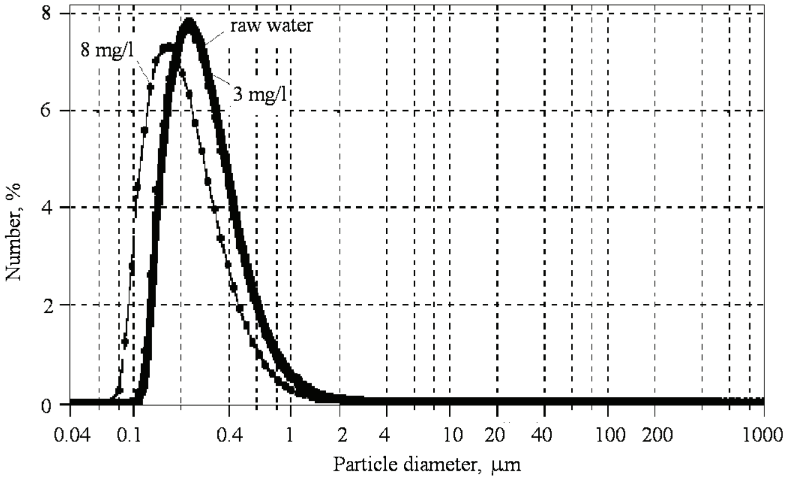


Fig. 5.32. Particle size distribution in raw wastewater and treated water.

5.7.2 Interaction with soluble organic matter

The number of experimental results described above point out that an interaction between the polyelectrolyte and the dissolved organic matter takes place. The experiments described in this section confirm the speculations about the polyelectrolyte - soluble organics interaction.

Fig. 5.33 illustrates the turbidimetric titration data. With increasing of the polyelectrolyte dosage the absorbance increases, that indicates a formation of complexes. The values of the absorbance are influenced by the size, the number and the structure of the complex particles formed (Buchhammer *et al.*, 2000). Since the molecular weight of the polymers tested is the same, the number of complexes at a certain polymer concentration is approximately the same. Therefore, the difference observed is due to the difference in the size and in the structure of complexes formed.

Fig. 5.34 illustrates the difference in the size of the complexes produced by the soluble organics and the different polyelectrolytes. The size of the complexes was measured at the excess of the soluble organics. There was observed that the complexes formed by PDADMAC are bigger than those formed by the poly-Amine. The reason for this difference is not clear. Several hypotheses may be suggested:

1. Since poly-amine has a higher charge density due to the space limitations some charges may be screened and excluded from the complex-formation by the large organic molecules. Therefore, despite the larger number of cationic groups per molecule the actual number of the groups able to participate in the complex formation is limited.
2. Hydrophobic part of the PDADMAC molecule can also interact with the hydrophobic organics and therefore, not only increase the range of the organics removed but also form larger complexes.

Some authors use the term “precipitation” to describe the reaction between a polyelectrolyte and soluble organics. The others use the term “complex-formation”. The second approach seems to be more correct. Since both the polyelectrolyte and the natural organic matter in wastewater are poly-ionic compounds, the solubility of the product is dependent upon the ratio between the polymer and the soluble organics in complex. Not only the solubility of the complex depends on the polyelectrolyte/organics ratio, but the size of the complexes depends on it as well.

Besides, it is very unlikely in such a complex system like wastewater that the polyelectrolyte will interact exclusively with the soluble organic matter. It is rather more realistic to assume that some segments of the polyelectrolyte are adsorbed on the suspended particle, while some others are involved in the complex formation with the organic matter.

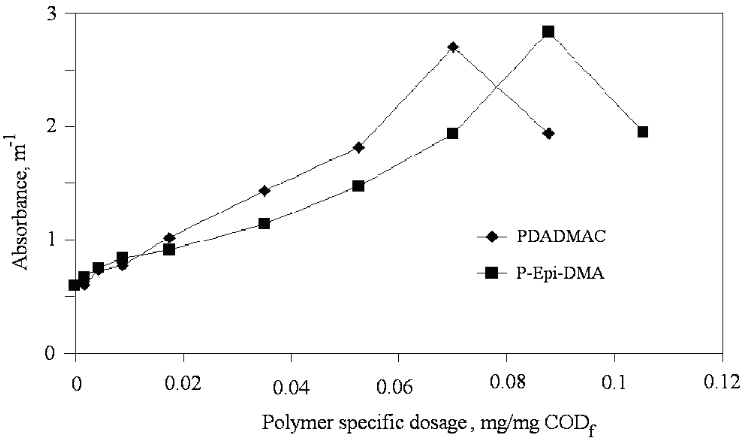


Fig. 5.33. Wastewater, filtered through 0,45μm membrane filter, titrated by PDADMAC and poly-amine, (λ = 420nm).

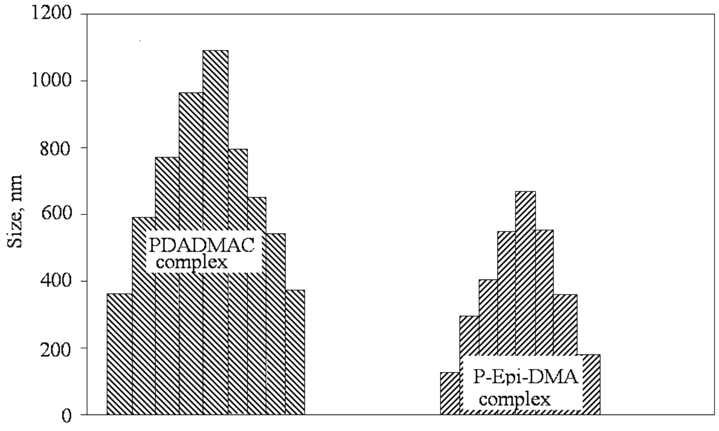


Fig. 5.34. Size of the polyelectrolyte-soluble organics complexes.

5.8 Residual polyelectrolyte

The residual concentration of the polyelectrolyte was determined in the coagulated sewage samples according to the methods described above. The eosin complex formation method was used for determination of the residual PDADMACs and the P-Epi-DMAs. The colloid titration was used for determination of the residual PAMs and PEs. The simple JAR test procedure was utilised, the sewage coagulated/flocculated by the polyelectrolyte was allowed to settle for 20 minutes and the supernatant was analysed for the residual polyelectrolyte.

Fig. 5.35 and Fig. 5.36 show the residual concentration of the PDADMAC and the P-Epi-DMA, respectively, as a function of dosage applied. The polyelectrolytes independently of the type exhibit the similar trend. The residual polyelectrolyte concentration in the filtered samples was significantly lower than in the non-filtered samples. The molecular weight has little effect on the residual polymer concentration, even at low dosage some difference was observed in the case of non-filtered samples. This difference became negligible at dosages higher than 3mg/l.

The large difference observed between the filtered and the non-filtered samples indicate that some amount of polymer associated with the particles or the soluble organic is still positively charged and, therefore, may be dangerous to the aquatic organisms. On the other hand, it is also possible that the complex between the polymer and the soluble organics is neutral, but due to higher stability constant of the polymer-eosin complex, the reaction goes towards formation of the latter. Therefore, the polymer, which normally would enter the environment as an inactivated compound, is determined as an active one.

The concentration of the residual polymer in the filtered samples is dependent on the dosage for all polymers tested. All polyelectrolytes show a flat region at low dosage, where most of the polyelectrolyte is adsorbed to solids or associated with organics and the amount of the free polymer in the solution is very low. However, at some concentration the further increases in doses result in the substantially greater residual polyelectrolyte concentration.

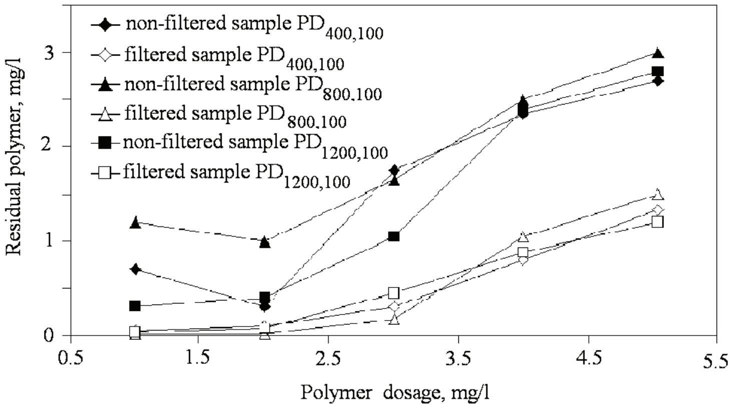


Fig. 5.35. Effect of PDADMAC dose and MW on residual polyelectrolyte concentration.

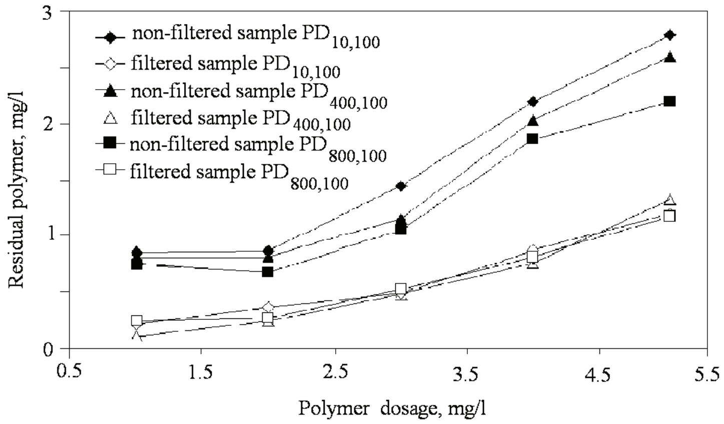


Fig. 5.36. Effect of poly-Amine dose and MW on residual polyelectrolyte concentration.

Fig. 5.37 illustrates the effect of the dosage on the residual polymer for poly-Acrylamide and poly-Etylenimin. The high molecular weight polyelectrolytes have lower residuals than the low molecular weight polymers at the same dosage. The effect of the type and the molecular weight was insignificant. Nevertheless, the residual polyelectrolyte concentration varies from polymer to polymer. This variance might by due to the different molecular weight distribution.

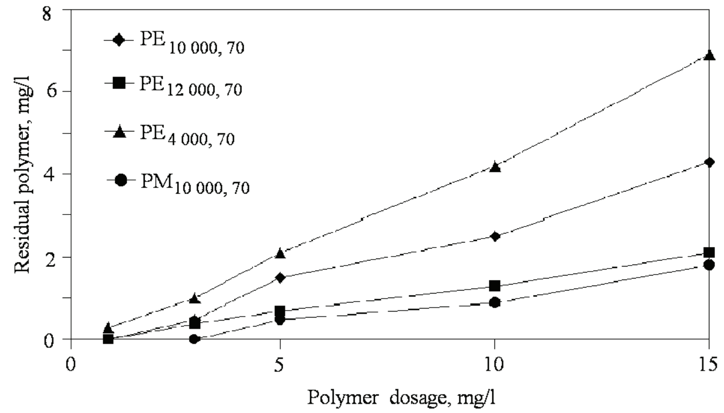


Fig. 5.37. Effect of high molecular weight polyelectrolyte dose on residual polyelectrolyte concentration.

Fig. 5.38 shows the effect of concentration of the stock polyelectrolyte solution on the residual polymer concentration. The more diluted polymer solution was used the higher concentration of the residual polyelectrolyte. This strange tendency can be explained by the polymers solution behaviour. It is well known that polymers form associates in solutions, probably, when introducing into the suspension some forces keep the pre-associated molecules together, by this improving adsorption and, therefore, reducing the residual polyelectrolyte. In the diluted polymer solutions association does not take place, leading in the end to a higher residual polymer concentration.

Fig. 5.39 illustrates the effect of the rapid mixing time and the intensity on the residual polymer concentration. The high mixing speed intensify the break-up of the flock and the polyelectrolyte desorption, leading to a lesser amount of the polymer adsorbed and the higher residual polyelectrolyte concentration. This effect is more pronounced with increasing of the rapid mixing intensity. As the data indicate, by reducing the rapid mixing time from 2 to 1 min one can reduce the residual polyelectrolyte concentration by more than 50%. The effect of the flocculation intensity was not so pronounced, but still by reducing the flocculation speed from 50 rpm to 20 rpm the residual polyelectrolyte concentration was reduced by 20%. Introducing tapered flocculation, 30% less polyelectrolyte was found in the liquid phase. The flocculation time did not have significant effect on the residual polyelectrolyte concentration.

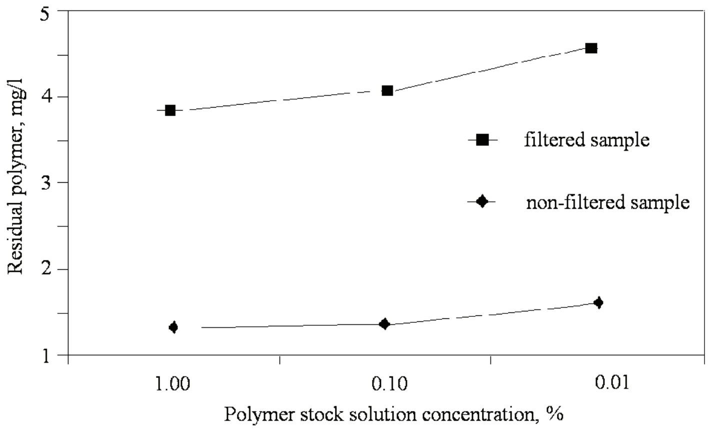


Fig. 5.38. Effect of polyelectrolyte stock solution on residual polyelectrolyte.

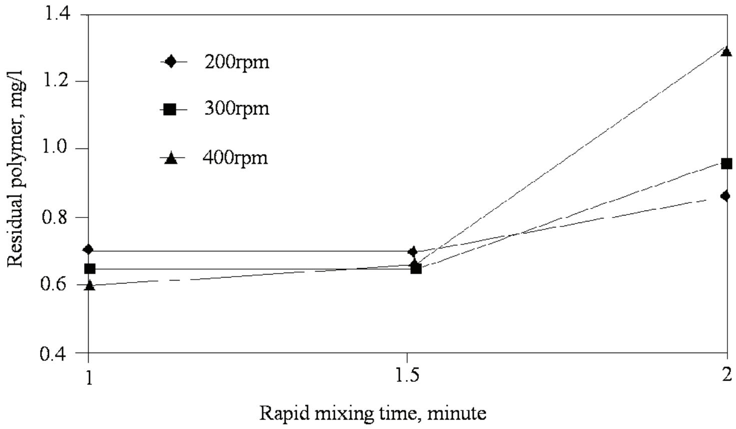


Fig. 5.39. Effect of rapid mixing time on residual polymer.

6 MODEL DEVELOPMENT FOR WASTEWATER COAGULATION-FLOCCULATION

A successful management of coagulation-flocculation of wastewater with polyelectrolytes depends on the possibility to predict an optimum dosage of the coagulant and the treatment efficiency. Therefore, this chapter is devoted to the discussion of the certain modelling techniques and development of an adequate model.

Several approaches are available for the modelling of the coagulation process. The experimental data described in chapter 5 provide information for the development of the mathematical as well as non-mathematical models.

A non-mathematical qualitative model provides an insight into the process and helps to understand and visualize the mechanism, but it does not give an opportunity to control and manage the process.

To control the coagulation process, one must obtain the quantitative mathematical model of the process. Therefore, it is necessary to analyze the relationships between the system variables and to obtain the mathematical model.

Since the idea of mathematical modelling is to establish a relationship between the input and the output variables, the modelling of a wastewater treatment process deals with establishing relationship between the characteristics of the inflow and the outflow. Fig. 6.1 schematically illustrates the input and the output of the wastewater coagulation model.

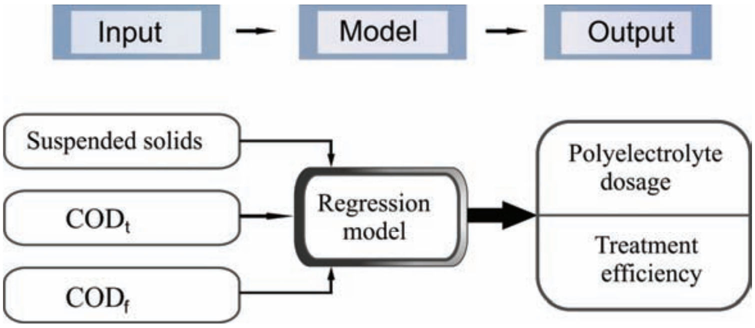


Fig. 6.1. Input and output of wastewater coagulation model.

Creation of a statistical model is the simplest solution, since the software “Unscrambler v 7.5”, which was used to design experiments, provides an excellent opportunity to use a variety of modelling methods. Such methods as the multiple linear regression, the principal component regression and the partial least square regression are available.

6.1 Descriptive model.

The polyelectrolyte introduced into wastewater interacts with the wastewater components. Fig. 6.2 schematically shows the main consumers of the polyelectrolyte. Any wastewater impurities possessing an anionic charge may interact with the polyelectrolyte. The mechanism of interaction depends on the colloidal properties of impurities.

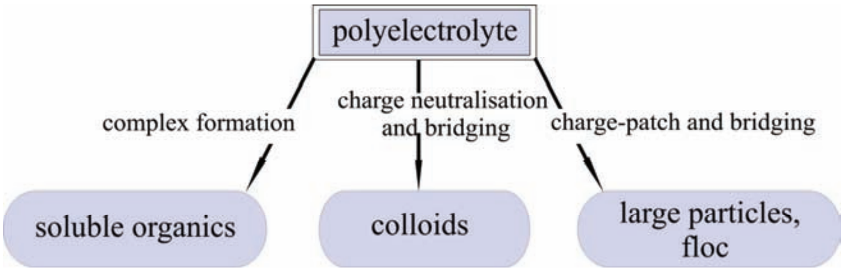
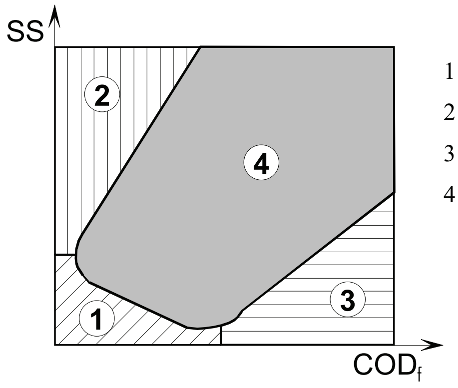


Fig. 6.2. Schematic representation of the consumption of polyelectrolyte during coagulation of wastewater.

The soluble organics interact with the polyelectrolyte via the complex formation. The colloidal particles are destabilised via the charge neutralisation and the bridging formation. The particles, which are much bigger than the polyelectrolyte molecule, are destabilised via the charge neutralisation.

The colloids in wastewater compete with the dissolved organics for the polyelectrolyte, when coagulating wastewater by the low molecular weight polyelectrolyte. The concentration ratio between SS and filtered COD determines which matter will be preferably removed. Fig. 6.3 illustrates the process of the wastewater coagulation.



1 - No aggregation;

2 - Preferential removal of colloids;

3 - Preferential removal of soluble organics;

4 - Competition between colloids and soluble organics.

Fig. 6.3. Schematic representation of suspended solids removal by polyelectrolytes in presence of dissolved organic matter.

Region 1 corresponds to a much diluted wastewater with a low concentration of SS and COD_f, this is a region where no visible aggregation occurs at any polyelectrolyte dosage. In the region 2 mostly the suspended matter is removed. In the region 3 mostly soluble organic matter is removed. In the region 4 the competition between the soluble organics and the suspended matter takes place.

6.2 Statistical regression model.

The program Unscrambler, which was used to design the experiments, provides a possibility to use a range of multivariate methods. The multivariate modelling involves relating of two sets of data, X and Y, by regression. The set X contains the independent variables, which in our case are the raw wastewater characteristics and the coagulant dosage. The set Y contains the response variables Y, which are the treated wastewater characteristics or the removal efficiencies.

Multiple linear regression (MLR) is a classical method that correlates a set of X variables to the corresponding Y values. In MLR a direct regression is performed between the X-matrix and Y.

$$Y = B_0 + B_1X_1 + B_2X_2 + \ldots + B_nX_n + f, \qquad \textit{eq. 6.1}$$

where B_i is a regression coefficient, f is Y-residuals.

The results of MLR model can be visualized with help of the response surface. The main disadvantage of the statistical model from the engineering point of view is that the coefficients do not have a physical meaning. Nevertheless, the removal efficiency and residual concentrations can be predicted with a great accuracy. It is also important to realize that a statistical model fails to predict if the raw water quality variations exceed

When the ratio COD_p/COD_f increases, i.e. the concentration of the particulate organic matter increases, the coefficient a decreases. The decrease of the coefficient a leads to faster "opening" of the parabola that is an extension of the destabilisation region. That corresponds well to the experimental and literature data (Veitser and Mints, 1984).

When the concentration of the colloidal and soluble organics increases, and the ratio COD_p/COD_f decreases the coefficient a increases. The increase of the coefficient a leads to a narrowed destabilisation region. Therefore, the coefficient a shows how wide the destabilisation region is.

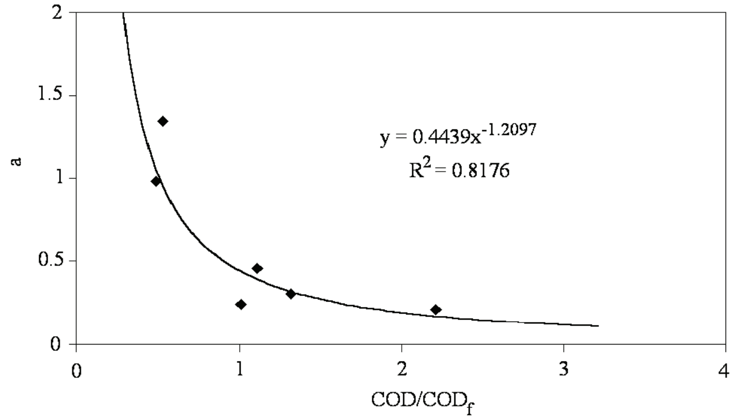


*Fig. 6.9. Coefficient **a** as a function of ratio between particulate COD and filtered COD (PDADMACs).*

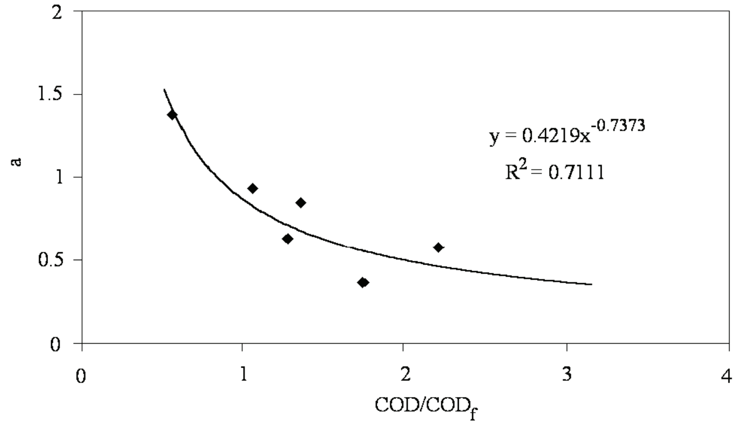


*Fig. 6.10. Coefficient **a** as a function of ratio between particulate COD and filtered COD (P-Epi-DMA).*

The coefficient ***b*** is always negative. Fig. 6.11 illustrates the variation of the coefficient ***b*** with the ratio between the particulate COD and the filtered COD.

The coefficient ***c*** in eq. 6.2 is a function of the initial wastewater turbidity and COD_f. In order to simplify the model the effect of COD_f on the coefficient ***c*** is neglected and coefficient ***c*** is assumed to be equal turbidity of the raw water.

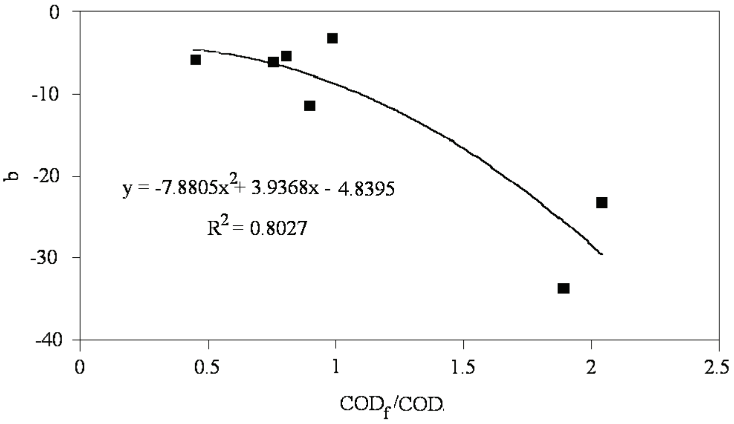


*Fig. 6.11. Coefficient **b** as a function of ratio between particulate COD and filtered COD (PDADMACs).*

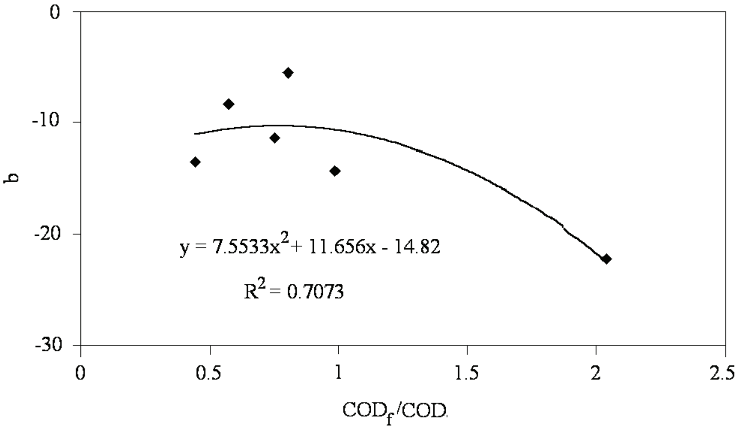


*Fig. 6.12. Coefficient **b** as a function of ratio between particulate COD and filtered COD (P-Epi-DMA).*

Substituting the coefficients ***a*** and ***b*** in eq. 6.6 with functions obtained gives:

for PDADMACs

$$D_{opt}=\frac{7{,}8805\left(COD_s/COD_p\right)^2-3{,}9368\left(COD_s/COD_p\right)+4{,}8395}{2\cdot 0{,}4449\cdot\left(COD_p/COD_s\right)^{-1{,}2097}} \qquad \text{eq. 6.7}$$

and for P-Epi-DMAs

$$D_{opt}=\frac{7{,}5533\left(COD_s/COD_p\right)^2-11{,}656\left(COD_s/COD_p\right)+14{,}82}{2\cdot 0{,}4219\cdot\left(COD_p/COD_s\right)^{-0{,}7373}} \qquad \text{eq. 6.8}$$

In chapter 5 was shown that a destabilization region is much wider when the high molecular weight polyelectrolytes are applied. Due to this the parabolic function is not applicable for description of coagulation with PAM and PE based polymers. With help of the least-squares method was determined that the best fit gives a power function with a negative exponent. Therefore, the turbidity of the treated water is described by following function:

$$\boldsymbol{T = aD^{-b}}, \qquad \text{eq. 6.9}$$

where $\boldsymbol{D}$ is the polyelectrolyte dosage ($\boldsymbol{D}\in[0.0001, 12]$), ***a*** and ***b*** are the coefficients. If the raw wastewater turbidity varies from 30 to 114 NTU (as was observed in the experiments) the coefficient $\boldsymbol{a} \approx$ ***constant***. The data indicate that $\boldsymbol{a} = 30$ gives satisfactory results.

The coefficient ***b*** depends on the initial turbidity. Fig. 6.13 illustrates the coefficient ***b*** as a function of the initial turbidity.

Therefore for the wastewater similar to those used in the experiments ($30<\text{Turbidity}_{\text{initial}}<114$) the following function may be adopted for calculation of the residual turbidity:

$$T=30D^{-0{,}411Ln(T_{in})+1{,}2786} \qquad \text{eq. 6.10}$$

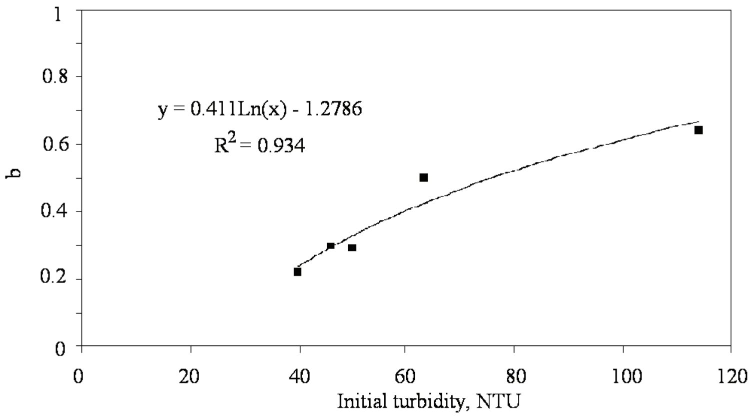


*Fig. 6.13. Coefficient **b** as a function of initial turbidity.*

6.4 Mathematical regression model. Polyelectrolyte and JKL as dual coagulant.

For the modelling of wastewater coagulation by the dual coagulant permission has been given to use the data obtained trough another project (Melin, 2006). These were used for validation of the model.

The wastewater coagulation by the dual coagulant, as well as by solo polyelectrolyte, can be described by the quadratic function (eq.6.2). The coefficients ***a***, ***b*** and ***c*** depend on the raw wastewater characteristics and dosage of JKL.

$a = f(COD_p/COD_f,$ *polyelectrolyte type dosage of JKL(mmol/l))*
$b = f(COD_p/COD_f,$ *polyelectrolyte type, dosage of JKL(mmol/l))*
$c = f(SS_{in},$ *dosage of JKL(mmol/l))*

The experimental results indicate that the effect of JKL dosage on the change of coefficients ***a*** and ***b*** is so significant, that the effect of the other factors can be neglected. This fact simplifies the model greatly.

Coefficient ***c*** changes linearly with JKL dosage as Fig. 6.14 illustrates. The absolute term in the equation is equal to the initial raw water turbidity, another coefficient is assumed to be constants if SSi is between 60 and 250 mg/l.

If the JKL concentration increases, the coefficient ***a*** increases as well. The increase of the coefficient ***a*** indicates the narrowing of the parabola. In the experiments it was observed as the narrowing of the destabilisation region with increasing the JKL dosage.

If we assume that the correlation between the value of the coefficient ***a*** and JKL concentration is linear, as illustrated by Fig. 6.15, the coefficient ***a*** can be expressed by the following:

*a = 7*JKL dosage(mmol/l) + 4,3* *eq. 6.10*

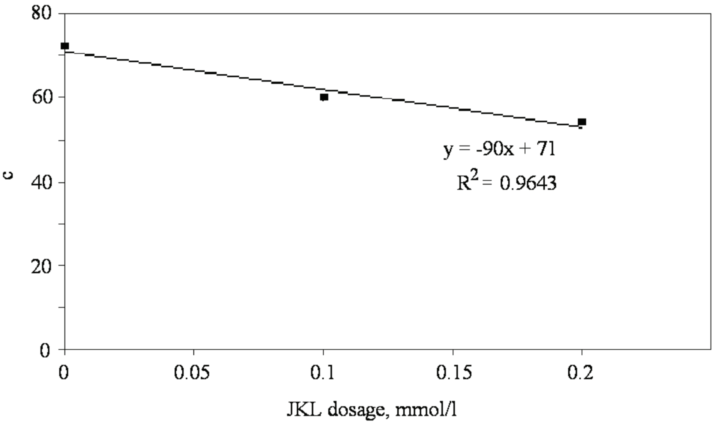


*Fig. 6.14. Coefficient **c** as a function of JKL dosage.*

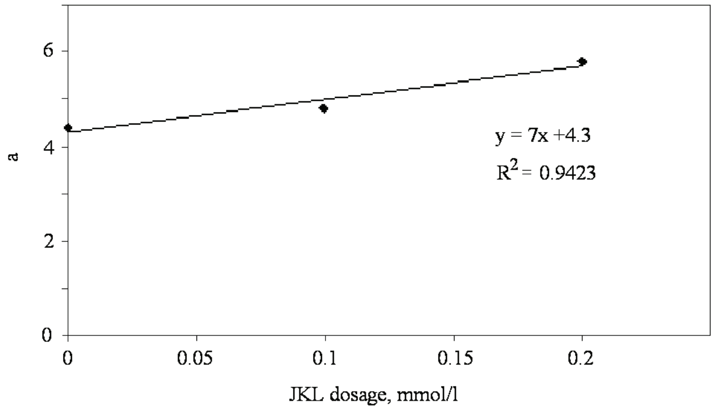


*Fig. 6.15. Coefficient **a** as a function of JKL dosage.*

The coefficient ***b*** is always negative. Fig. 6.16 illustrates the variation of the absolute value of the coefficient ***b*** with the JKL dosage. The coefficient ***b*** is expressed by the following function:

*b = 47*JKL dosage(mmol/l) + 20,1* *eq.6.11*

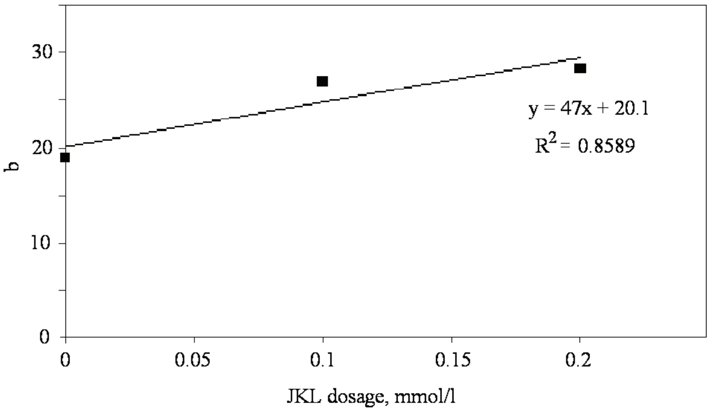


Fig. 6.16. Coefficient ***b*** *as a function of JKL dosage.*

Substituting the coefficients ***a, b*** and ***c*** in eq. 6.2 with functions obtained gives turbidity:

$$T = (7*JKL + 4,3)*D^2-(47*JKL+20,1)*D -90*JKL+71, \qquad eq.6.12$$

where

JKl is the dosage of JKL (mmol/l),
D is the dosage of polyelectrolyte (mg/l),
T_i is the initial turbidity (NTU).

Substituting the coefficients ***a*** and ***b*** in eq. 6.6 with functions obtained gives the optimum polyelectrolyte dosage:

$$D_{opt}= \frac{47*JKL+20{,}1}{2*(7*JKL+4{,}3)}, \qquad eq.6.13$$

where *JKl* is the dosage of JKL (mmol/l),

6.5 Validation of mathematical regression models.

The prediction ability of the model can be tested on a new data set that has not been used during development of the model. The validation set should be chosen from the same population as the calibration set. The test set is not identical to the calibration set, but all parameters of these two sets are otherwise to be as similar as possible. Therefore, to satisfy these conditions, the three different sets of coagulation data were used.

6.5.1 Polyelectrolyte as solo coagulant

The optimum polyelectrolyte dosage (D_{opt}) was calculated for different COD_p/COD_f. The calculated D_{opt} is plotted against experimental D_{opt} in Fig. 6.17. Error bars shown in Fig. 6.17 correspond to 10% error. It is evident that the model allows us to predict the optimum dosage with 90% accuracy for the most cases considered. All the points fall within 85% accuracy.

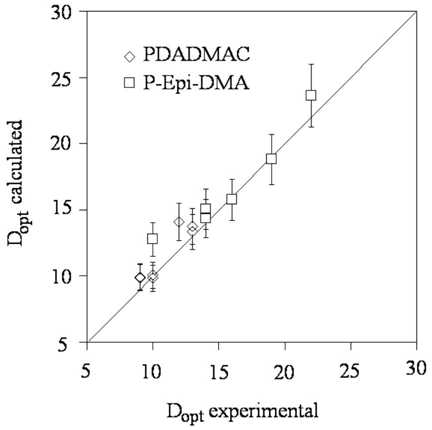


Fig. 6.17. Calculated value D_{opt} versus optimum dosage of polyelectrolyte observed in the experiments.

According to eq. 6.10 the residual turbidity was calculated and plotted against the residual turbidity results obtained in the experiments, as Fig. 6.18 illustrates. The error bars shown in Fig. 6.18 correspond to the 10% error. It is evident that the model allows us to predict the residual turbidity with 90% accuracy for the most cases considered. All points fall within 80% accuracy.

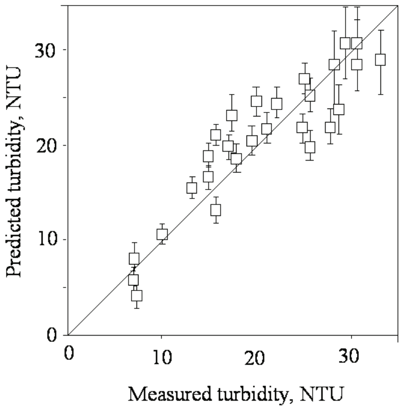


Fig. 6.18. Predicted turbidity versus measured turbidity.

The results of the external validation have shown that both models can be used for prediction of optimum dosage and residual turbidity with 80% accuracy.

6.5.2 Dual coagulant

The residual turbidity was calculated according to the eq. 6.12. The data obtained are plotted against the experimental data in Fig. 6.19. The error bars correspond to the 15% error. The validation of the model revealed that the model allows us to predict the residual SS concentration with 90% accuracy if the following conditions are satisfied:

- JKL dosage between 0 and 0,2 mmol/l
- Polymer dosage between 0 and 3 mg/l
- Initial SS concentration between 60 and 180 mg/l

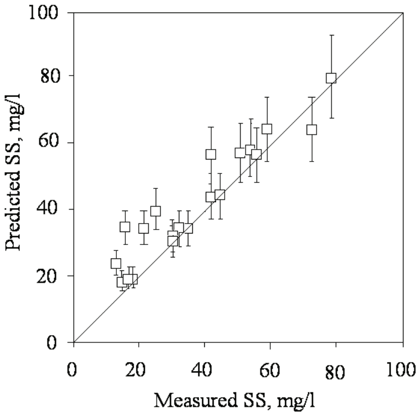


Fig. 6.19. Predicted SS versus measured SS.

7 ANALYSIS AND RECOMMENDATIONS

7.1 Revising hypotheses

The results described in chapter 5 allow us to check the validity of the hypotheses that were suggested a priory in chapter 3.

Hypothesis 1 stated: *The quality of raw wastewater, especially SS and COD concentrations, affects polyelectrolyte consumption and treatment efficiency.*

The experimental results support this hypothesis. The effect of the quality of raw wastewater on the polyelectrolyte consumption and treatment efficiency is significant. It was found that the specific optimum dosage of polyelectrolyte is affected by the concentration of the particles and colloids as well as the soluble organic matter.

The increase of particulate matter concentration has a following effect on the coagulation-flocculation with polyelectrolytes:

- decrease of the specific optimum dosage
- increase of the removal efficiency and improvement of the supernatant quality
- widening of the destabilisation region (low molecular weight polyelectrolytes)
- the soluble organic matter concentration had a negative effect on the treatment efficiency; it is also characterised by the increased optimum dosage (low molecular weight polyelectrolytes)

The increase of the dissolved organic matter concentration has the following consequences on the coagulation-flocculation with polyelectrolytes:

- increase of the specific optimum dosage
- deterioration of the supernatant quality
- shrinkage of the destabilisation region

Further **Hypothesis 1** stated that *polyelectrolyte dosage and treatment efficiency can be predicted based on the raw water quality parameters, such as turbidity, suspended solids concentration and COD.*

Both mathematical and statistical regressions can be utilised for the description of wastewater coagulation-flocculation process. The obtained experimental data was satisfactory described using the statistical multilinear regression model as well as the mathematical regression model. The models allowed prediction of the optimum polyelectrolyte dosage with less than 15% error.

Hypothesis 2 stated: *Soluble organic matter may negatively affect the coagulation flocculation process, leading to the higher polyelectrolyte dosages and the poor quality of the treated water.*

This hypothesis is only partially supported by the experimental data. The concentration of the soluble organic matter had a negative effect on the performance of the low molecular weight polyelectrolytes as solo coagulants. It was found that the interaction between the low molecular weight polyelectrolyte and the dissolved organic matter led to complex formation, observed as colloidal particles. It was found that the size of particles produced depends on the concentration ratio polyelectrolyte/dissolved organics. The amount of particles smaller than 0.3 μm increases as a result of complex formation between polyelectrolyte and soluble organics.

Hypothesis 3 stated: *The amount of charge is a key factor governing coagulation-flocculation process i.e. the differences observed in the action of different polyelectrolytes at the same dosage are due to the different amount of charge introduced.*

This hypothesis is supported by experimental results. The zero value of zeta-potential was observed at dosages lower than the optimum flocculation concentration. It was found that independently of polyelectrolyte type the increase of molecular weight leads to the particle destabilisation at lower dosage. A high concentration of soluble organic matter led to increased polyelectrolyte consumption. The zero zeta-potential was reached at higher dosages.

Hypothesis 4 stated: *The molecular weight of polyelectrolyte is an important polyelectrolyte characteristic to ensure flocculation and particle separation. Medium to high molecular weight polyelectrolytes produce settleable floc.*

The effect of molecular weight within each polymer type was investigated but the size of the aggregates depended on the polyelectrolyte dosage rather then on molecular weight of polyelectrolytes. The biggest floc was obtained at the dosage lower than the optimum. The flocculation rate increases with increasing polymer dosage to a certain level after that further increase is impossible. The higher the concentration of the particulate matter in the raw wastewater, the bigger floc was formed at the same polyelectrolyte dosage.

Hypothesis 5 stated: *Combined use of low dosage of the inorganic coagulant and the polyelectrolyte may give a good particle accompanied by a phosphate removal and low sludge production.*

This hypothesis is supported by the experimental results. Combined coagulant demonstrated excellent particles and colloids removal efficiency. The dual coagulants

(JKL and high molecular weight polymers) demonstrated good ortho-phosphate removal efficiency. Sludge production /SS removal ratio was reduced by 20-30% compare to only inorganic coagulant.

Hypothesis 6 stated: *The particle size distribution changes during coagulation/flocculation with polyelectrolytes. Polyelectrolytes interact with soluble organic matter producing tiny unsettleable floc.*

The experimental results have confirmed this hypothesis. The interaction between the polyelectrolyte and the dissolved organic matter leads to production of precipitate. The size of the particles produced depends on the concentration ratio polyelectrolyte/dissolved organics. The size of the aggregates depends on the polyelectrolyte dosage. The largest floc is obtained at the dosage lower than the optimum. During coagulation-flocculation with the low molecular weight polyelectrolytes the particle size distribution of the wastewater changes. The number of the particles smaller than 0.3μm increases as a result of the complex formation between the polyelectrolyte and the soluble organics.

Hypothesis 7 stated: *At the optimum conditions (optimum dose, mixing and flocculation) the residual polyelectrolyte concentration is minimal.*

The residual polymer concentration is a function of the dose for each polyelectrolyte tested. Depending on the dose applied the residual polymer concentration varies from 20 to 50% (at the optimal or lower polymer dosage). The molecular weight within one type of polyelectrolyte has little effect on residual polyelectrolyte concentration. The PAMs and PEs have lower residuals than PDADMACs and P-Epi-DMAs.

7.2 Polyelectrolyte selection principles

Based on the results obtained in the coagulation-flocculation-settling of municipal wastewater by cationic organic polyelectrolytes, the following recommendations for polyelectrolyte selection can be given:

The experimental results have shown that the quality of wastewater has the greatest influence on the process mechanism. Though, both the removal efficiency and the polyelectrolyte optimum dosage are affected by concentration of the particulate and dissolved matter.

- Based on the experimental results the combined coagulant should be recommended in cases of wastewaters with low SS content (SS<100mg/l). The concentrated wastewaters successfully coagulated by polyelectrolyte alone. The type of polyelectrolyte plays a minor role. Therefore the choice of product should be based on economical and technological evaluations. Generally, the 100% charged polyelectrolytes (PDADMAC and P-Epi-DMA types) are recommended at molecular weight higher than 400000g/mol.

- The high molecular weight polyelectrolytes (PAM and PE) of medium to high charge density can be equally effective. When combined with low dosage inorganic coagulant, highly charged polyelectrolytes performed better.

- Since the specific dosage is reduced with increasing SS concentration the treatment of concentrated wastewater is economically more beneficial.

- The low molecular weight polyelectrolytes provide the removal of particles and COD_f. Therefore, they should be chosen in cases when the chemical treatment is the most advanced stage of the treatment sequence.

- The method used for separation of the coagulated particles affects the choice of the polyelectrolyte. The high molecular weight polyelectrolytes produce large floc, which settles more rapidly. For the sludge blanket separation, filtration or dissolved air flotation the low molecular weight polyelectrolytes are quite satisfactory alternative.

- The treatment and handling of the sludge generated in the coagulation-flocculation process are important aspects to consider when choosing the products to be used as coagulants.

- Considering sludge production, the PAM based polyelectrolytes were found to be most suitable solo coagulants if only particulate matter is to be removed. If both particles and organic matter are to be removed, the polyelectrolyte of choice would be a PDADMAC based product.

- Considering both particle removal and organic matter removal, the most suitable solo coagulant would be PDADMAC based product. When also phosphate has to be removed, a combined coagulant should be used and in this case. The combination giving least amount of sludge seems to be JKL/PDADMACs.

7.3 Economic evaluation

A simple evaluation of an economic aspect is performed. It was shown above that polyelectrolytes perform as well as inorganic coagulants, but whether or not polyelectrolytes will be accepted as primary coagulants depends on the economic benefits.

The price for the polymeric organic coagulant containing 20-40% of active compound is 15 NOK/kg (Kemira).

That makes the price for the active compound:

X= 100*price of product/concentration of product=100*15/40=37,5NOK/kg

At the dosage 10 mg/l the price of treatment of 1 m^3 of wastewater is:
Dosage = $10g/m^3$
Price = 0,01kg*37,5 NOK/kg = 0,375 NOK/m^3

The price for a JKL product is 900NOK/tonn (Kemira), therefore the price for the treatment with JKL at dosage 1 mmol/l will be $0,33NOK/m^3$.

The price for combined use of polyelectrolyte at dosage 3 mg/l and JKL at dosage 0,2mmol/l will be $0,18NOK/m^3$.

Therefore, the combined use of JKL and polyelectrolyte gives significant reduction in price for the reagents. The additional benefits can arise from the reduction of amount of sludge to handle.

8 CONCLUSIONS

The results of this thesis show that synthetic organic polyelectrolytes are effective coagulants for wastewater treatment. Both low and high molecular weight cationic polyelectrolytes can be used as solo primary coagulants and combined with low dosage inorganic coagulant.

- The optimum dosage of the low molecular weight polyelectrolyte (PDADMAC and P-Epi-DMA) is affected by the concentration of the particles, colloids and soluble organic matter. The specific dosage is significantly reduced with increasing concentration of the particulate matter. The soluble organic matter has a negative effect on the treatment efficiency and increases the optimum dosage.
- The residual polyelectrolyte concentration is a function of dosage for each polyelectrolyte tested. The molecular weight within one type of polyelectrolyte has little effect on the residual polyelectrolyte concentration. High molecular weight polyelectrolytes (PAM and PE) have lower residuals than the PDADMACs and P-Epi-DMA. The optimisation of the rapid mixing and flocculation procedures is crucial for minimising residual polymer concentration.
- The process of wastewater coagulation-flocculation by the low molecular weight polyelectrolytes can be satisfactory described using a statistical multilinear regression model and mathematical regression model. The model allows prediction of the optimum dosage with 85% accuracy for both PDADMACs and P-Epi-DMA.
- The process of wastewater coagulation-flocculation by the high molecular weight polyelectrolytes can be described by the function $T = aD^{-b}$. The coefficients a and b are functions of the raw wastewater characteristics. The model allows predicting the residual turbidity with 80% accuracy.
- Addition of a low dosage of inorganic salt (i.e. Fe) significantly improves suspended particles and colloids removal by polymers. The combined coagulant removes the ortho-phosphates as well. Coagulation by such a dual coagulant is satisfactory described by the mathematical regression model. The treatment efficiency can be predicted with 90% accuracy.
- The zero value of zeta-potential was observed at dosages lower than that of optimum flocculation concentration. Independently of type of polyelectrolyte the increase of molecular weight leads to particle destabilisation at lower dosage. A high concentration of soluble organic matter leads to increased polyelectrolyte consumption. In such cases the zero zeta-potential is reached only at at elevated polyelectrolyte dosages.
- The interaction between polyelectrolyte and dissolved organic matter lead to production of complexes, observed as colloidal particles. The size of the particle aggregates produced depends on the concentration ratio polyelectrolyte/dissolved organics. The amount of particles smaller than 0,3µm increases with increasing amount of dissolved organic matter as a result of complex formation between polyelectrolyte and the soluble organics.
- The size of aggregates depends on polyelectrolyte dosage. The biggest flocs are obtained at the dosage lower than that of the optimum. The flocculation rate increases with increasing of polymer dosage to a certain level after which further increase is impossible. The higher the concentration of particulate matter in the raw wastewater, the bigger is the floc formed at the same polyelectrolyte dosage. A low dose of inorganic salt (dual coagulant) significantly increases the rate of polymer adsorption and floc size.

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SAMMENDRAG

Kjemisk rensing er en velkjent teknikk for rensing av avløpsvann. Den brukes både alene og som forbehandling foran biologiske rensetrinn. Til tross for mange fordeler assosiert med kjemisk rensing er denne teknikken uønsket på grunn av høy slamproduksjon. Siden den overskytende mengde slam er utfelt metallhydroksid/fosfat, kan en delvis eller fullstendig erstatning av metallkoagulant med syntetisk organisk koaguleringsmiddel redusere slamproduksjon betydelig.

Denne avhandlingen undersøker muligheter for bruk av syntetiske organiske polymerer for rensing av kommunalt avløpsvann.
De første to kapitlene av avhandlingen gir innblikk i forskningsresultater og teoretisk bakgrunn for bruk av polymerer for koagulering.
Hypoteser er lagt frem i det tredje kapittelet.
Det fjerde kapittelet beskriver forsøksplanlegging, analytiske metoder og prosedyrer brukt i forsøk.
Forsøksresultater er lagt frem og diskutert i kapittel 5.
I kapittel 6 blir forholdet mellom polymertype, kvaliteten på avløpsvann og renseeffekt etablert. Disse sammenhengene er vist i modeller.
Kapittel 7 inneholder hypoteseanalyse og veiledning for valg av polymer som hovedkoagulant.
Følgende konklusjoner er trukket fram i det avsluttende kapittel 8:

Syntetiske organiske polymerer viste seg å være effektive koagulanter for kommunalt avløpsvann. Både høymolekylærvekt og lavmolekylærvekt polymerer kan brukes alene og i kombinasjon med uorganiske koagulant.

Konsentrasjon av både partikulært, kolloidal og løselig organisk materiale i råvann påvirker optimaldose for polymer samt renseeffekten. Den spesifikke polymerdosen reduseres med økning av partikkelkonsentrasjon, derimot vil en økning av konsentrasjon av løselig organisk materiale føre til økning av optimale polymerdoser.

Kombinasjon av lav dose av uorganisk koagulant (dvs. Fe) og polymer fører til en betydelig forbedring av renseeffekten. I tilleg vil den sammensatte koagulanten felle ut fosfater. Tilsetning av uorganisk koagulant fører til økning av både polymeradsorpsjonshastighet og fnokkstørrelse.

Både statistisk regresjonsmodell og matematisk regresjonsmodell kan brukes for å beskrive koagulering med syntetiske organiske polymerer. De foreslåtte modellene gir mulighet for å forutsi renseeffekt og optimalt koagulantdose med minst 80% nøyaktighet.

Restpolymerkonsentrasjon er en funksjon av polymerdose. Optimalisering av polymer blandings- og flokkuleringsparametrer er viktig for minimalisering av restpolymerkonsentrasjon.

APPENDIX

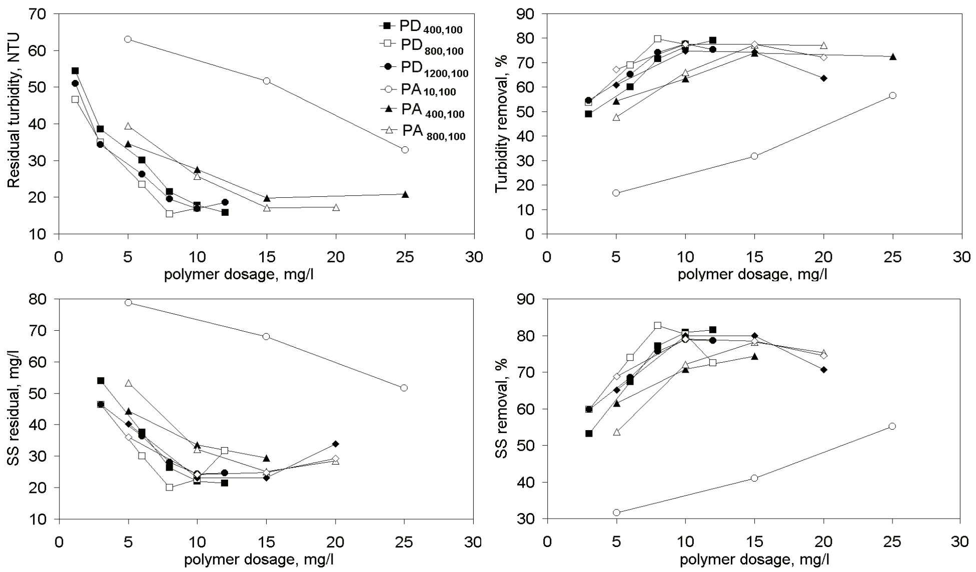


Fig. 1. Turbidity and SS removal by low molecular weight polyelectrolytes.

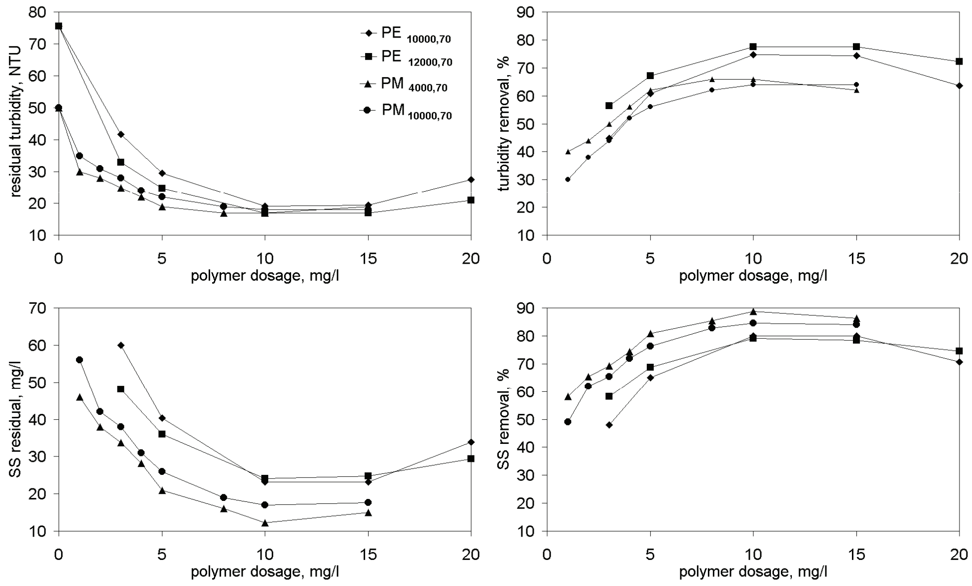


Fig. 2. Turbidity and SS removal by high molecular weight polyelectrolytes.

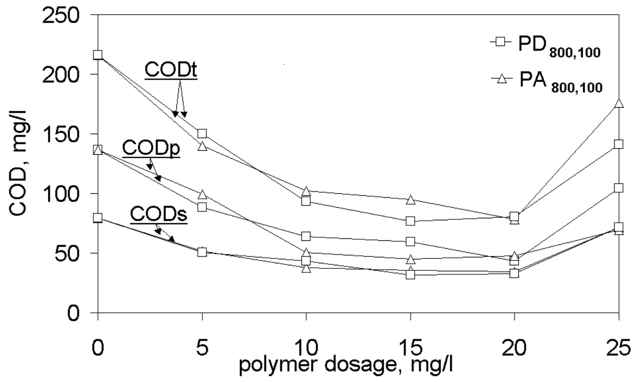


Fig. 3. COD removal by low molecular weight polyelectrolytes.

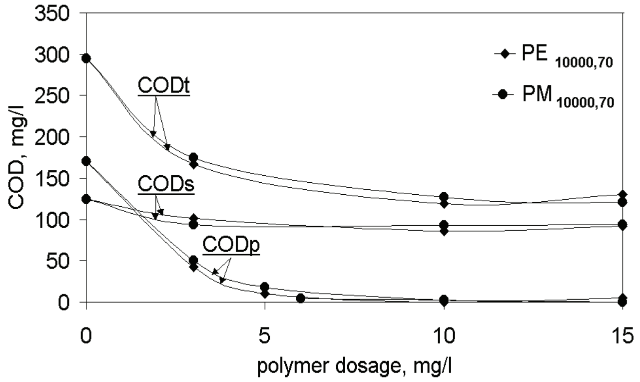


Fig. 4. COD removal by high molecular weight polyelectrolytes.

Table 1. COD removal when municipal wastewater was coagulated by cationic polyelectrolytes combined with JKL.

Polymer	Polymer dose (mg/l)		Removal (%)			
			COD total		COD_f	
	JKL 0.1 mmol/l	JKL 0.2 mmol/l	JKL 0.1 mmol/l	JKL 0.2 mmol/l	JKL 0.1 mmol/l	JKL 0.2 mmol/l
$PD_{400, 100}$	3	2	76	88	21	32
$PD_{800, 100}$	2	3	86	90	27	31
$PD_{1200, 100}$	1	1	83	88	26	30
$PA_{10, 100}$	3	2	61	63	26	28
$PA_{400,100}$	3	3	62	64	25	24
$PA_{800, 100}$	3	2	59	61	24	35
$PM_{10000,40}$	4	3	53	66	3	12
$PM_{10000,70}$	4	3	63	64	2	4

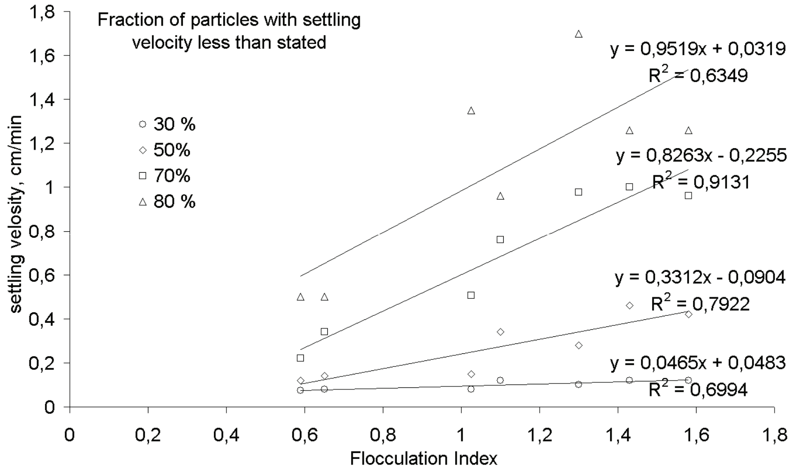
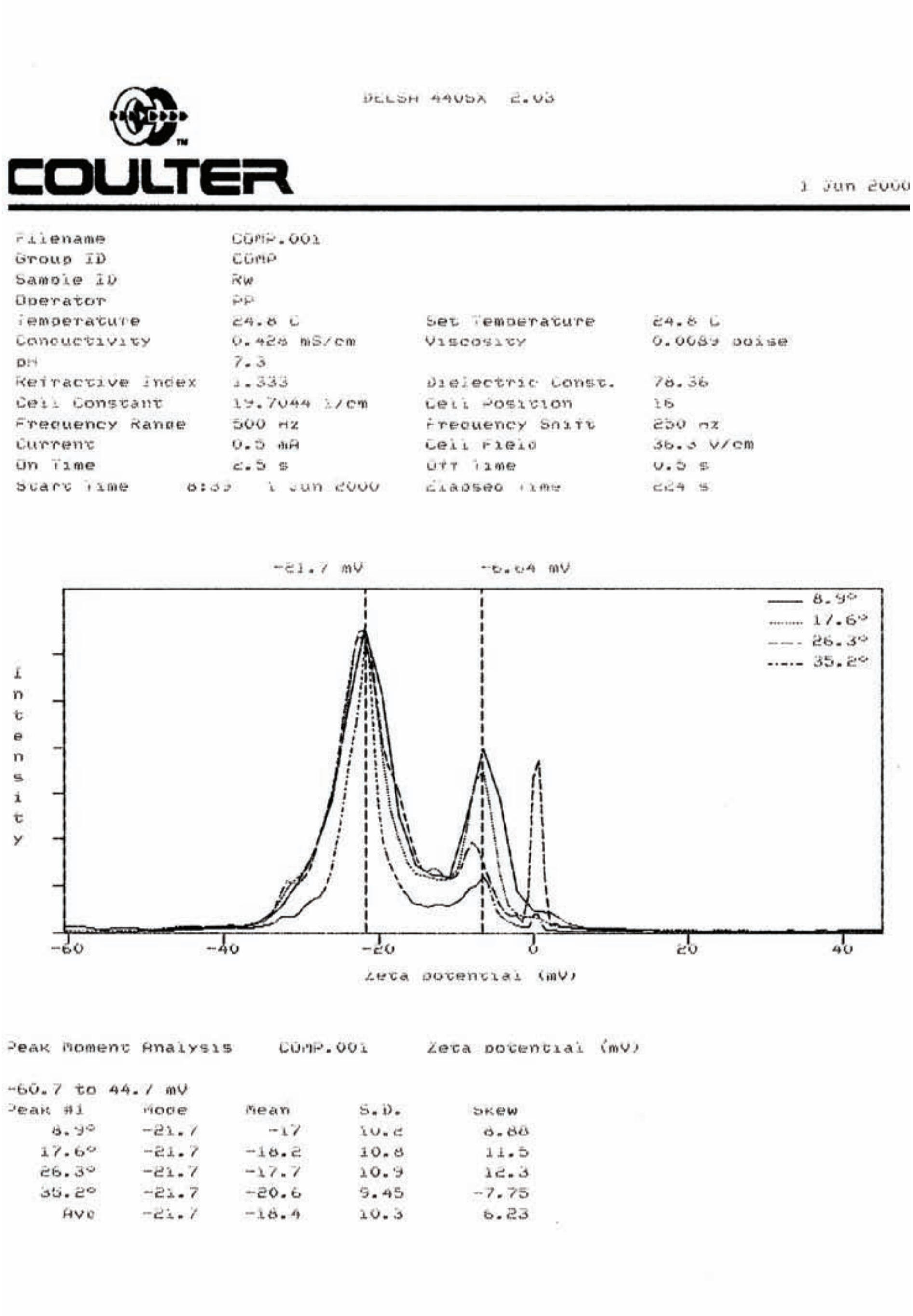


Fig.5. Relationship between flocculation index and settling velocity of aggregates.

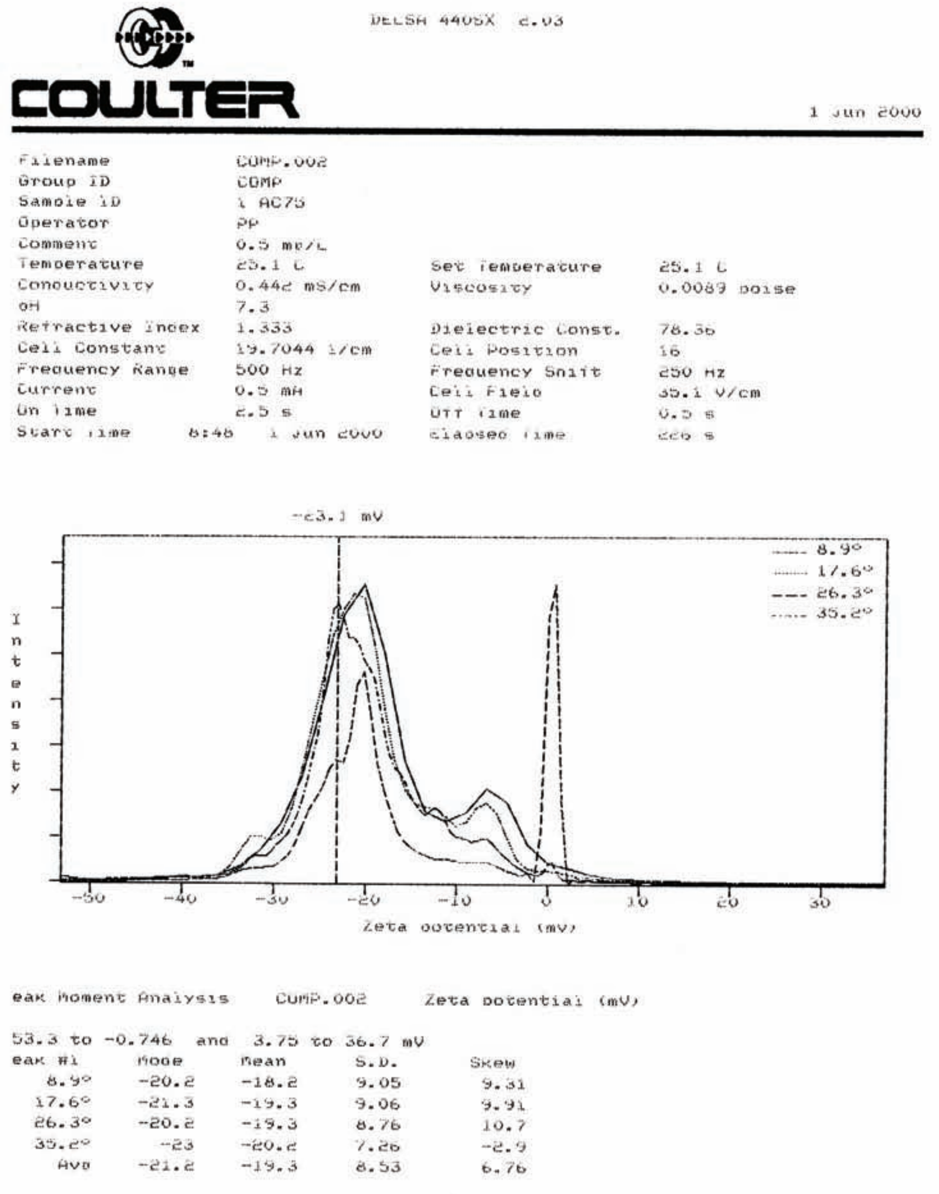


```
                              DELSA 440SX  2.03
COULTER
                                                                      1 Jun 2000

Filename              COMP.001
Group ID              COMP
Sample ID             Rw
Operator              PP
Temperature           24.8 C              Set Temperature       24.8 C
Conductivity          0.428 mS/cm         Viscosity             0.0089 poise
pH                    7.3
Refractive Index      1.333               Dielectric Const.     78.36
Cell Constant         19.7044 1/cm        Cell Position         16
Frequency Range       500 Hz              Frequency Shift       250 Hz
Current               0.5 mA              Cell Field            36.3 V/cm
On Time               2.5 s               Off Time              0.5 s
Start Time      8:33   1 Jun 2000         Elapsed Time          224 s
```

```
Peak Moment Analysis     COMP.001       Zeta potential (mV)

-60.7 to 44.7 mV
Peak #1         Mode       Mean        S.D.        Skew
      8.9°     -21.7        -17        10.2        8.88
     17.6°     -21.7      -18.2        10.8        11.5
     26.3°     -21.7      -17.7        10.9        12.3
     35.2°     -21.7      -20.6        9.45       -7.75
       Ave     -21.7      -18.4        10.3        6.23
```

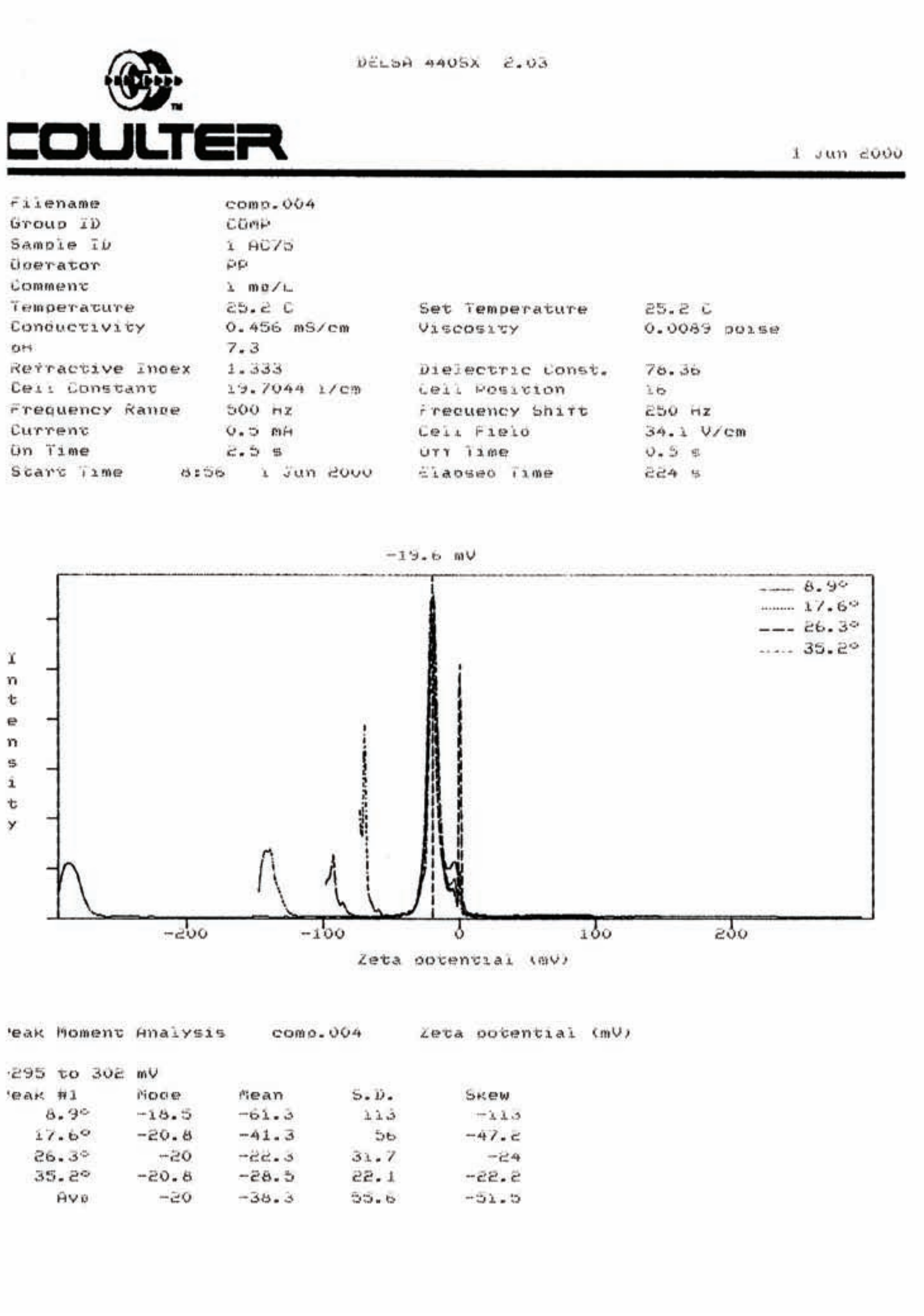


```
COULTER                    DELSA 440SX  2.03
                                                                1 Jun 2000

Filename               COMP.002
Group ID               COMP
Sample ID              1 AC75
Operator               PP
Comment                0.5 mg/L
Temperature            25.1 C             Set Temperature        25.1 C
Conductivity           0.442 mS/cm        Viscosity              0.0089 poise
pH                     7.3
Refractive Index       1.333              Dielectric Const.      78.36
Cell Constant          19.7044 1/cm       Cell Position          16
Frequency Range        500 Hz             Frequency Shift        250 Hz
Current                0.5 mA             Cell Field             35.1 V/cm
On Time                2.5 s              Off Time               0.5 s
Start Time        8:48    1 Jun 2000      Elapsed Time           226 s
```

```
eak Moment Analysis      COMP.002       Zeta potential (mV)

53.3 to -0.746  and  3.75 to 36.7 mV
eak #1        Mode       Mean        S.D.        Skew
    8.9°      -20.2      -18.2       9.05         9.31
   17.6°      -21.3      -19.3       9.06         9.91
   26.3°      -20.2      -19.3       8.76        10.7
   35.2°        -23      -20.2       7.26        -2.9
     Avg      -21.2      -19.3       8.53         6.76
```



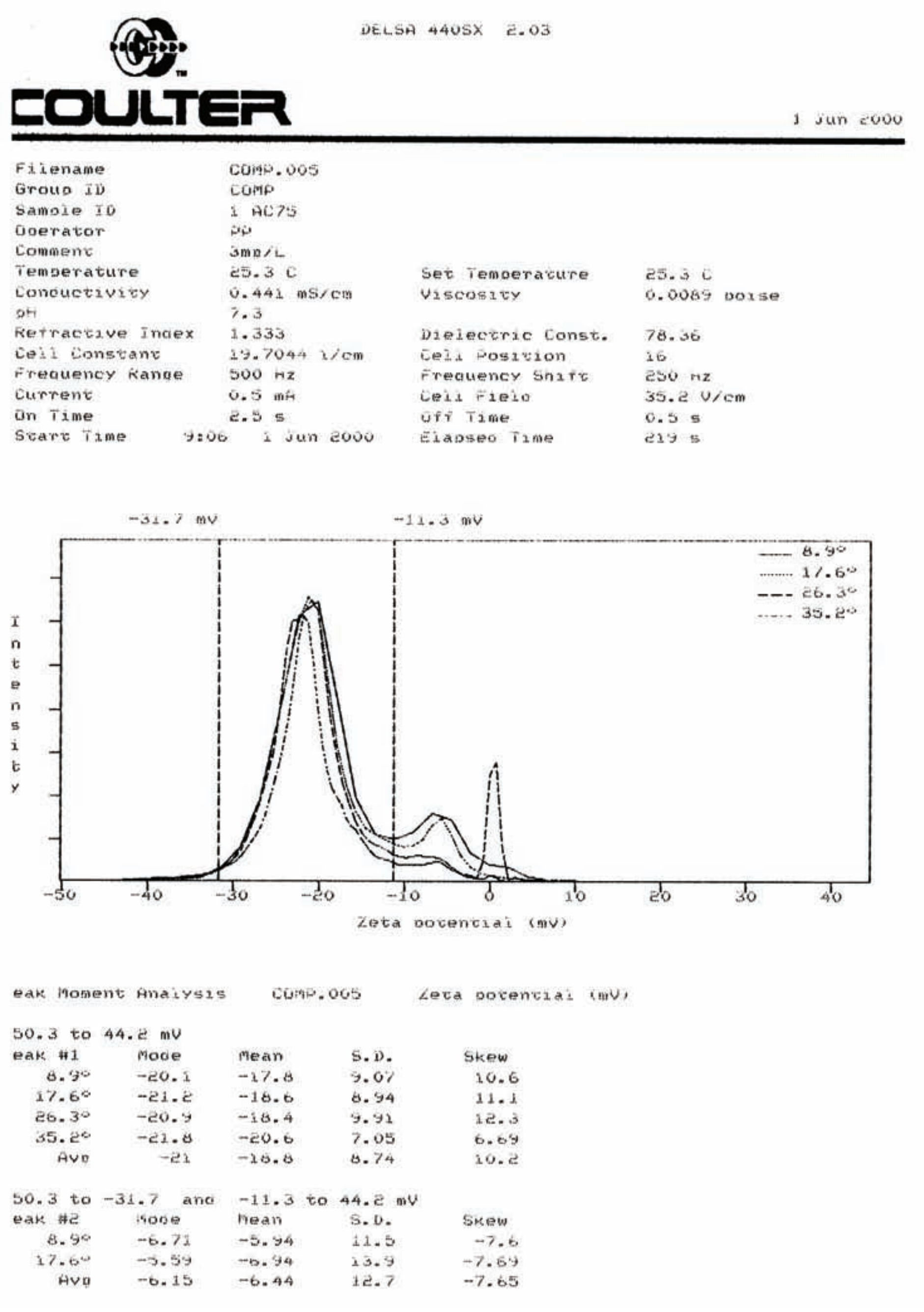
```
                              DELSA 440SX  2.03

COULTER                                                            1 Jun 2000

Filename              comp.004
Group ID              COMP
Sample ID             1 AC75
Operator              PP
Comment               1 mg/L
Temperature           25.2 C                 Set Temperature      25.2 C
Conductivity          0.456 mS/cm            Viscosity            0.0089 poise
pH                    7.3
Refractive Index      1.333                  Dielectric Const.    78.36
Cell Constant         19.7044 1/cm           Cell Position        16
Frequency Range       500 Hz                 Frequency Shift      250 Hz
Current               0.5 mA                 Cell Field           34.1 V/cm
On Time               2.5 s                  Off Time             0.5 s
Start Time      8:56    1 Jun 2000           Elapsed Time         224 s

eak Moment Analysis     comp.004      Zeta potential (mV)

295 to 302 mV
eak #1        Mode       Mean       S.D.       Skew
    8.9°     -18.5      -61.3        113       -113
   17.6°     -20.8      -41.3         56      -47.2
   26.3°       -20      -22.3       31.7        -24
   35.2°     -20.8      -28.5       22.1      -22.2
     Avg       -20      -38.3       55.6      -51.5
```



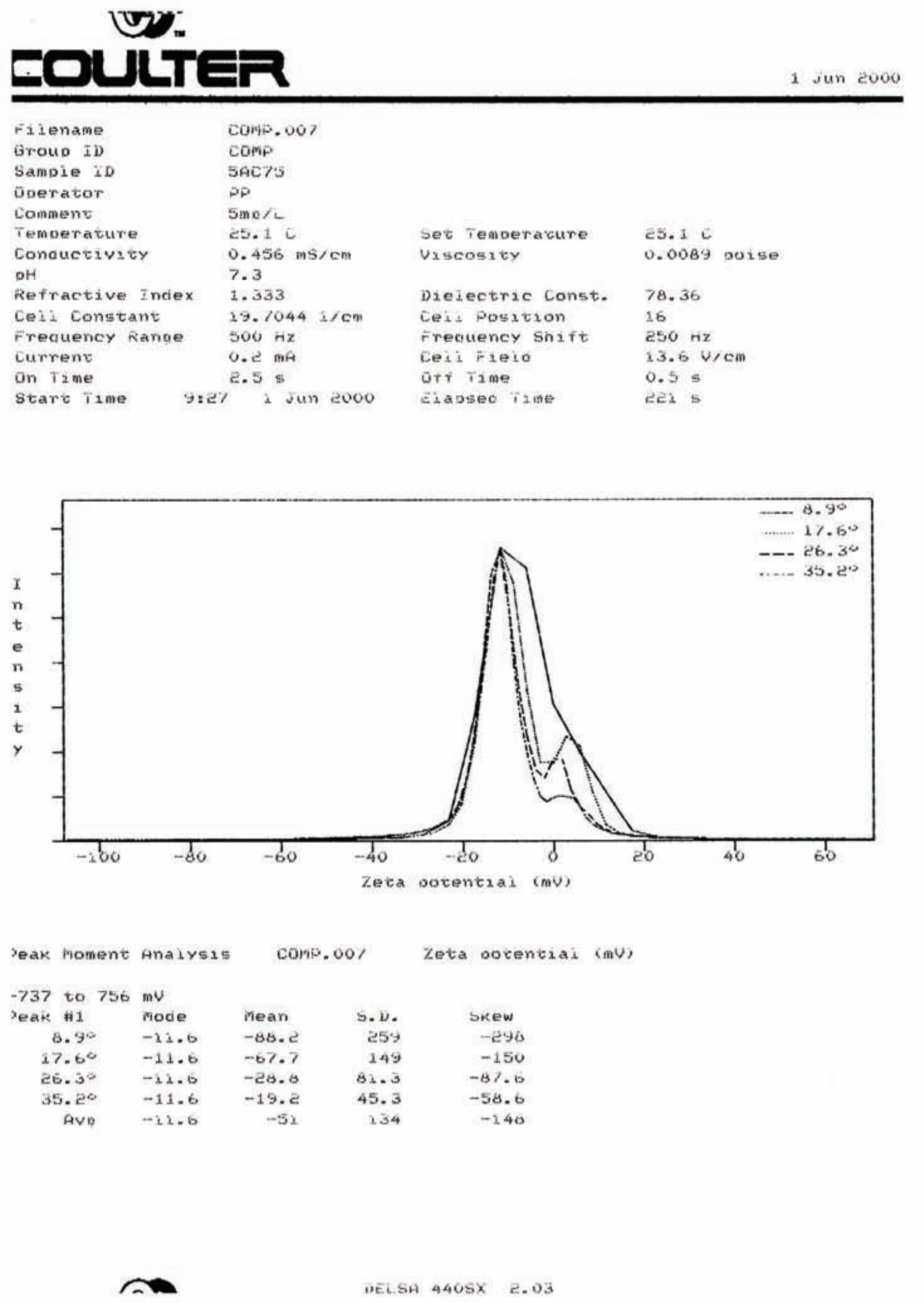
```
                              DELSA 440SX  2.03
COULTER
                                                                      1 Jun 2000

Filename             COMP.005
Group ID             COMP
Sample ID            1 AC75
Operator             pp
Comment              3mg/L
Temperature          25.3 C             Set Temperature       25.3 C
Conductivity         0.441 mS/cm        Viscosity             0.0089 poise
pH                   7.3
Refractive Index     1.333              Dielectric Const.     78.36
Cell Constant        19.7044 1/cm       Cell Position         16
Frequency Range      500 Hz             Frequency Shift       250 Hz
Current              0.5 mA             Cell Field            35.2 V/cm
On Time              2.5 s              Off Time              0.5 s
Start Time       9:06   1 Jun 2000      Elapsed Time          219 s
```

```
eak Moment Analysis     COMP.005      Zeta potential (mV)

50.3 to 44.2 mV
eak #1        Mode       Mean       S.D.       Skew
   8.9°      -20.1      -17.8       9.07       10.6
  17.6°      -21.2      -18.6       8.94       11.1
  26.3°      -20.9      -18.4       9.91       12.3
  35.2°      -21.8      -20.6       7.05       6.69
    Avg        -21      -18.8       8.74       10.2

50.3 to -31.7  and  -11.3 to 44.2 mV
eak #2        Mode       Mean       S.D.       Skew
   8.9°      -6.71      -5.94       11.5       -7.6
  17.6°      -5.59      -6.94       13.9      -7.69
    Avg      -6.15      -6.44       12.7      -7.65
```



COULTER 1 Jun 2000

```
Filename             COMP.007
Group ID             COMP
Sample ID            5AC75
Operator             PP
Comment              5mg/L
Temperature          25.1 C               Set Temperature      25.1 C
Conductivity         0.456 mS/cm          Viscosity            0.0089 poise
pH                   7.3
Refractive Index     1.333                Dielectric Const.    78.36
Cell Constant        19.7044 1/cm         Cell Position        16
Frequency Range      500 Hz               Frequency Shift      250 Hz
Current              0.2 mA               Cell Field           13.6 V/cm
On Time              2.5 s                Off Time             0.5 s
Start Time      9:27   1 Jun 2000         Elapsed Time         221 s
```

```
Peak Moment Analysis     COMP.007     Zeta potential (mV)

-737 to 756 mV
Peak #1        Mode       Mean       S.D.       Skew
    8.9°      -11.6      -88.2        259       -298
   17.6°      -11.6      -67.7        149       -150
   26.3°      -11.6      -28.8       81.3      -87.6
   35.2°      -11.6      -19.2       45.3      -58.6
     Avg      -11.6        -51        134       -148
```

DELSA 440SX 2.03