

# Optimisation of the coagulation process to improve plant availability of phosphorus in wastewater sludge

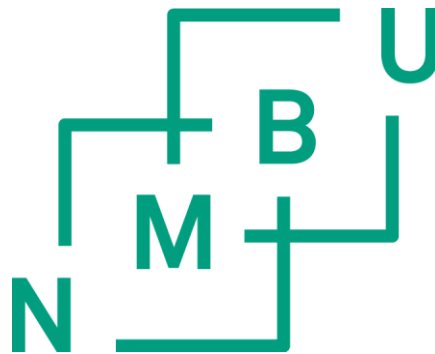
Optimalisering av kjemisk fellingsprosess for å forbedre plantetilgjengelighet av fosfor i avløpsslam

Doctor of Philosophy (PhD) Thesis

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*Dedicated to*

*My mother, a strong and gentle soul who taught me to believe  
in hard work and that so much could be done with little*

*My grandmother for being my first teacher*

*My late father for earning an honest living for us and for  
supporting and encouraging me to believe in myself*

*My Punchi for being my guardian during my educational  
career*

## Summary

Coagulation is used for the removal of colloids, particles and phosphates in wastewater treatment. The efficiency and economics of chemical coagulation, one of the most robust wastewater treatment processes, is critically dependent on the optimal coagulant dosage. The main challenge is to determine the optimal coagulant dosage relative to rapidly varying influent. Excessive coagulant overdosing leads to increased treatment costs and high amount of sludge production, while underdosing leads to a failure to meet the water quality targets alongside less efficient operation of the treatment plant. A fully automated, advanced dosing control system (ACDS) based on all parameters critical for the coagulation process is the answer for this challenge. DOSCON AS has developed an ACDS previously tested and elaborate by Lu (2003) and Rathnaweera (2010). This study starts with a hypothesis that efficient dosing control systems should be capable of adjusting to treatment efficiencies and increased capacities while keeping the dosages at a minimum. Current research expand the capabilities of the ACDS to address more stringent treatment requirements while keeping the dosages low and treatment efficiencies evenly good. The full scale tests of ACDS studies were carried out at NRA wastewater treatment plant in Norway, and the ability to increase treatment capacities from 700 L/s to 1300 L/s and treatment efficiencies from 94% to 96% of total phosphates are demonstrated.

Global mineral phosphate reserves are rapidly depleting, therefore all phosphorus sources must be utilized and reused. Wastewater sludge alone represents an important source of phosphorus. The value of fertilizer can be affiliated to the plant availability of phosphorus (PAP). The measurement of PAP is complex, but research has proposed that aluminium content in sludge is inversely proportional to the PAP (Øgaard, 2013). Thus, the intention of this research is to search for concepts that reduce the aluminium content in sludge to increase PAP. Lab scale coagulation experiments were carried out to investigate the factors that may reduce aluminium content in sludge, an important factor that influences the PAP.

The impact of OH/Al ratio in coagulants was studied. While the aluminium content in sludge increased with the increase of OH/Al of coagulants, plant growth tests suggested the opposite under the same conditions. These observations challenged the existing understanding of the inverse proportionality between the aluminium content in the sludge and PAP. The form of the aluminium species in coagulated sludge is supposed to vary with the coagulant type, particle and phosphate content etc., and may have different impacts on PAP. This may

explain the observed discrepancies, and the further insight to the chemistry of Al-P bonds and Al-OH bonds may be valuable.

When an inorganic coagulant is added to wastewater, a portion of aluminium will engage in hydrolysis reaction while the rest will react with phosphates. The ratio between these fractions are influenced by the OH/Al ratio of coagulants and the particle and phosphate content in wastewater. Organic cationic coagulants are able to efficiently remove particles. Therefore, a pre-coagulation with cationic coagulants is expected to reduce the portion of inorganic coagulants engaged in hydrolysis and reduce the total consumption of aluminium. Such a concept should reduce the content of aluminium in sludge, which should lead to increased PAP. This possibility is launched as the second hypothesis in this thesis.

The results and analysis of this research could not reject the first hypothesis on the capability of ACDS to generate sludge with least aluminium content, i.e. highest possible PAP. However, the results rejected the second hypothesis of the possibility to efficiently and universally substitute inorganic coagulants with cationic polymers as an operational option. Hence, reducing aluminium content in sludge to gain higher PAP is rejected to be valid at all instances. It works under certain conditions, but the effect of substitution is found to be far less than anticipated in working conditions and ranges.

However, a better insight to the mechanism of coagulation and speciation in sludge is recommend as important steps to improve the PAP without post treatment of sludge. Additional research is recommended to quantify Al-P bonds and Al-OH bonds in the sludge.

## Sammendrag

Koagulering brukes for fjerning av kolloider, partikler og fosfater i avløpsvannbehandling. Effektiviteten og økonomien ved kjemisk felling, en av de mest robuste rensesprosesser for avløp, er kritisk avhengig av optimal dosering av koagulant. Hovedutfordringen er å finne den optimale koagulantdosen relativt til en raskt varierende innløpskvalitet. Overdosering av koagulanter fører til økte kjemikaliekostnader og høy slamproduksjon, mens underdosering fører til en dårligere vannkvalitet og mindre effektiv drift av rensenanlegget. Et helautomatisk, avansert dosering kontrollsystem (ADCS) basert på alle parametere som er kritiske for koaguleringsprosessen er svaret på denne utfordringen. DOSCON AS har utviklet et ACDS som har blitt testet og dokumentert av Lu (2003) og Rathnaweera (2010). Denne PhD studien starter med en hypotese om at effektive doserings kontrollsystemer (ACDS) skal være i stand til å tilpasse seg å øke behandlingseffektivitet og kapasitetsøkning, mens dosering holdes på et minimum. Denne studien utdyper og utvider mulighetene til ACDS å møte strengere renskrav med lavest mulige doser og jevnlig behandlingseffektivitet. Fullskala tester av ADCS studier ble gjennomført ved NRA rensanlegg i Norge, og evnen til å øke behandlingseffektiviteten fra 700 l / s til 1300 l / sek og oppnå behandlingseffektivitet fra 94% til 96% av totale fosfater er demonstrert.

Verdens tømmes fortløpende for mineral fosfatreserver, dermed må alle fosforkilder utnyttes og gjenbrukes. Avløpsslam representerer en av de viktigste kildene til fosfor. Verdien av slam som gjødsel kan være tilknyttet til plantetilgjengeligheten av fosfor (PAP). Måling av PAP er komplisert, men det eksisterer dokumentasjon på at aluminiuminnholdet i slammet er omvendt proporsjonal med PAP (Øgaard, 2013).

Laboratorieskala koagulasjonsforsøk ble utført for å undersøke de faktorer som kan redusere innholdet av aluminium i slammet, en viktig faktor som påvirker PAP.

Virkningen av OH /Al-forhold i koagulanter ble studert. Mens innholdet av aluminium i slammet økte med økningen av OH / Al av koagulanter, konkluderte vekst forsøkene det motsatte under visse forhold. Dette utfordret den etablerte forståelsen om omvendt proporsjonalitet mellom aluminiuminnholdet i slam og PAP. Fordi former av aluminiums artene i koagulert slam kan variere med koagulanttype, partikkel- og fosfatinnhold osv., kan det ha forskjellige virkninger på PAP. Dette kan forklare de observerte avvik, og gi ytterligere innsikt og verdifulle forklaringer om kjemien i Al-P bindinger og Al-OH bindinger.

Når et uorganisk koaguleringsmiddel tilsettes avløpsvann vil en del av aluminium delta i hydrolysereaksjonen, mens resten vil reagere med fosfater. Forholdet mellom disse fraksjonene blir påvirket av OH / Al-rasjon mellom koagulanter, partikler og fosfatinnholdet i avløpsvann. Da organiske kationiske koagulanter effektivt fjerner partikler kan det forventes at en pre-koagulasjon med kationiske koagulanter vil redusere andelen av uorganiske koaguleringsmidler som deltar i hydrolysen, og dermed redusere det totale forbruket av aluminium. Et slikt konsept skal redusere innholdet av aluminium i slammet som skal lede til øket plantetilgjengelighet av fosfor. Denne muligheten er lansert som den andre hypotesen i avhandlingen.

Resultatene og analysene av denne forskningen kan ikke forkaste den første hypotesen om evnen til ACDS å generere slam med minst aluminiuminnhold, dvs. høyest mulig plantetilgjengelighet av fosfor. Men resultatene forkaster den andre hypotesen om muligheten for effektivt å erstatte uorganiske koagulanter med kationiske polymerer, for å redusere innholdet av aluminium i slammet som fører til høyere plantetilgjengelighet av fosfor, selv om det er tilfellet i noen situasjoner. Det fungerer på visse vilkår, men effekten av substitusjon er funnet å være langt mindre enn forventet på vanlige arbeidsområder.

En bedre innsikt i mekanismen for koagulering og aluminiumsformene i slam er anbefalt som viktige tiltak for å forbedre plantetilgjengelighet av fosfor uten etterbehandling av slam. Ytterligere forskning er anbefalt innen å kvantifisere Al-P bindinger og Al-OH bindinger i slammet.



## List of abbreviations

ACN	Adsorption-Charge Neutralisation
ADCS	Advanced dosing control system
ALS	Aluminium Sulphate
ANFIS	Adaptive Network based Fuzzy Interference System
ANN	Artificial Neural Network
BA	Biomass Allocation
BOD	Biochemical Oxygen Demand
CDCS	Coagulant Dosing Control System
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DWTP	Drinking Water Treatment Plant
FLC	Fuzzy Logic Controller
Me	Metal
MLP	Multilayer Perceptron
NOM	Natural Organic Matter
NRA	Nedre Romerike Avløpsselskap
Ortho-P	Orthophosphate
P	Phosphate
PACl	Polyaluminium Chloride
PAP	Plant Availability of Phosphorus
PCA	Principal Component Analysis
PLSR	Partial Least Squares Regression
SCD	Streaming Current Detector
SS	Suspended Solids
SWF	Sweep Flocculation
SWWTP	Skipphelle Wastewater Treatment Plant
Total-P	Total Phosphorus
TUO	Effluent turbidity
UV	Ultraviolet
WW	Wastewater
WWTP	Wastewater Treatment Plant

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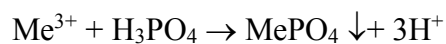
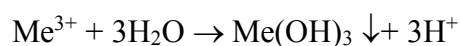
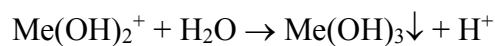
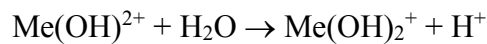
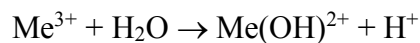
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# 1. Introduction.

## 1.1 The process of coagulation

Global trends over the last decades with increasing urbanization, population growth and industrialization have led to surface water resources facing considerable pressures. In this context, wastewater treatment has become one of the most important management actions to reduce pollution of natural water resources.

Coagulation is an established process for transforming colloids and smaller particles into larger aggregates for subsequent phase separation, mostly through sedimentation, flotation or filtration. Coagulation targets the colloid particles of size  $10^{-7}$  to  $10^{-4}$  mm in diameter (Sahu and Chaudhari 2013). Thus, it can efficiently remove particulate matter, colour, some toxic materials and microorganisms in drinking water. The main purpose of coagulation in domestic wastewater treatment is to remove particulate fractions of organic matter, phosphates, nitrogen as well as dissolved phosphates (P). The main chemical reactions during chemical coagulation of wastewater can be described by the following equations, where Me represents metal ions which could either be aluminium (Al) or iron (Fe):



The hydrolysis process takes place through many intermediate species depending on the pH (Baes and Mesmer 1976). This process produces metal hydroxides as sludge while reducing the pH. The latter could be an advantage for wastewaters with high pH/alkalinity as it creates optimal coagulation pH ranges, and conversely a disadvantage for waters with low pH/alkalinity as it may reduce the pH too much. The reduction of pH may also be a disadvantage for subsequent processes such as biological treatment.

Four mechanisms are widely accepted as dominating in wastewater coagulation: double layer compression, adsorption - charge neutralization, inter-particle bridging and

sweep floc. The sweep-floc mechanism is identified as the dominating mechanism in coagulation of domestic wastewater (Metcalf & Eddy 2003).

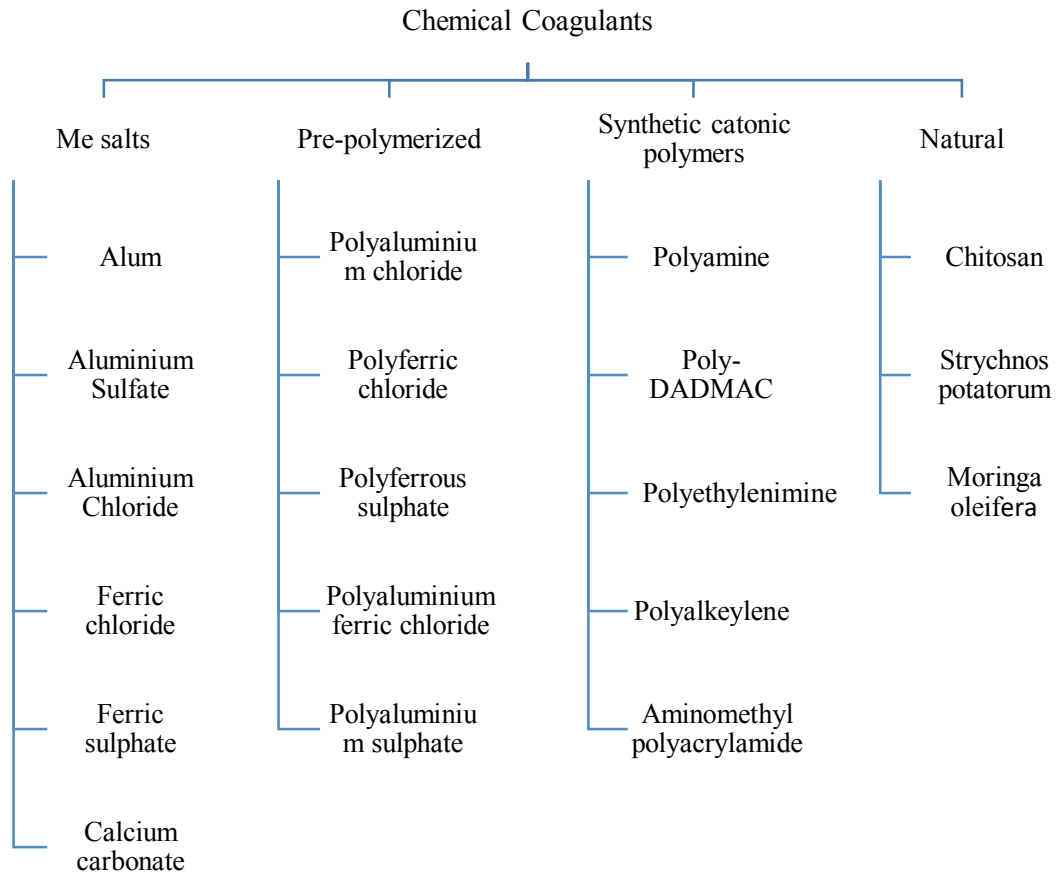
Due to the combined mechanism of precipitation, adsorption on to hydroxides and removal as colloids/particles, coagulation can remove phosphates beyond 95%. However, coagulation is not efficient for the removal of dissolved organic matter or dissolved nitrogen. The latter can be removed with biological processes, thus the widespread use of combined biological-chemical processes today.

The optimal coagulation in wastewater depends on the coagulant dosage appropriate for the given water quality, coagulant type and separation conditions. The optimal coagulant dosage is mainly a function of the wastewater flow, pH, particles and phosphates (Ratnaweera et al. 1994). The production of hydroxide sludge is considered as a challenge in coagulation, which can be optimized using better dosing control systems (Ratnaweera and Fettig 2015).

In wastewater treatment, it is necessary to combine proper wastewater treatment processes, a dosing control system, coagulant type and dosing method to achieve the required particle and P removal efficiencies to obtain high quality sludge. The investigation of those factors in the coagulation process and quantitative explanations are the main aims of this research work.

## 1.2 New developments in coagulation process.

The complex of different interconnected parameters influences on the process of chemical coagulation. Thus, it is important to determine the efficiency of the coagulants in the coagulation process under specific conditions (Verma et al. 2012). Depending on the effectiveness of the water treatment process, coagulants can be classified as:



**Figure 1.** Categorization of chemical coagulants according to their effectiveness (after Verma et al. 2012).

Pre-polymerized metal salts usually show more effectiveness in suspended solids (SS) removal in comparison to metal salts such as aluminium sulphate, ferric chloride and ferric sulphate (Ratnaweera 1992; Jiang and Graham 1998). It has also been reported that pre-polymerized coagulants such as PACl, Polyaluminium ferric chloride, Polyferrous sulphate and Polyferric chloride are not only more effective in SS and particular P removal but also produce less sludge volumes, even in low temperatures (Gregory and Rossi 2001). The research of the SS and particular P removal efficiencies showed that the pre-polymerized coagulants resulted in faster flocculation and stronger flocs comparing to the alum at the equivalent dosage (Verma et al. 2012). Most of the industrial and domestic wastewaters are negatively charged, thus it is better to use cationic polymer instead of anionic and non-ionic polymers for better particle and Total-P removal efficiency (Verma et al. 2012). Nevertheless, the mechanism of this process is not yet well understood.

A number of new coagulants are emerging. Jarvis (2012) compared novel Zr and traditional coagulants Fe and Al to reduce the Me content in the coagulated sludge. According



to a comparison of Zr coagulant with traditional coagulant Fe, the Zr coagulant provides much better particle and Total-P reduction. In addition, floc properties are significantly improved with larger and stronger flocs forming when the Zr coagulant is used. (Jarvis et al. 2012). Furthermore, the required dosage of Zr to achieve required treatment efficiency is much lower than traditional coagulants. The reason for this reduced dosage is high valence (Jarvis et al. 2012).

The combination of new and existing coagulants and/or producing hybrid coagulants have become popular in recent years with development of new technologies. Zhang (2014) compared aluminium sulfate and PAC with the new inorganic-organic hybrid material coagulant zirconium-glycine complex (ZGC) in terms of treated water quality and flocs properties. Results show that turbidity removal is higher when using ZGC coagulation (93,8 %) compared to other commonly used coagulants. The predominant mechanism of coagulation using ZGC is determined as the charge neutralization. The usage of ZGC coagulant improves the growth rate of aggregated flocs and good recovery ability of flocs compared to traditional coagulants. Zhang (2014) has reported that the largest floc size was achieved within 5 min, the hydraulic retention time decreases and removal efficiency increases.

In 2012, Zhang investigated fouling control and phosphorus removal by applying in-line coagulation prior to ultrafiltration to treat domestic wastewater. The filterability improves after coagulation, which is contributed to biopolymer removal and the formation of larger particles. Adding more  $\text{FeCl}_3$  and  $\text{AlCl}_3$  reduces the development rate of trans-membrane pressure (TMP), demonstrating less membrane fouling. Changing PACl dosage shows only little effect on the variation of TMP increase rate. With respect to phosphorus removal, dosing  $\text{FeCl}_3$  and  $\text{AlCl}_3$  achieves higher removal efficiency than using PACl (Zheng et al. 2012).

The removal of P from wastewater using a combination of open gradient superconducting magnetic separation (OGMS) and high gradient superconducting magnetic separation (HGMS) was investigated by Zhao in 2012. The magnetic seeding material used was  $\text{Fe}_3\text{O}_4$ , and a novel composite inorganic coagulant was added to combine the P with the magnetic seed. The important parameters that influenced the removal efficiency of P in OGMS or HGMS, such as slow mixing time, magnetic seeding dosage, coagulant dosage, hydraulic retention time, magnetic field strength and flow rate, were systematically investigated. The performance of the OGMS–HGMS process was evaluated by treating P in synthetic wastewater. The results show that all of the investigated parameters except for slow mixing time, has a significant effect on P removal. Overall, the use of OGMS as a pretreatment

for HGMS is shown to be a good method of increasing P removal efficiency while simultaneously increasing the flow rate of HGMS (Zhao et al. 2012).

Apart from novel coagulants, combination of unit process, coagulants and factors like temperature and retention time influence the treatment efficiency (Ong et al. 2005). Hence, the optimization of these factors may significantly increase the process efficiency. Different coagulants affect different degrees of destabilization. The higher the valence of the counter ion, the higher the destabilizing effect, and consequently a lesser dose is needed for coagulation (Birjandi et al. 2013).

The focus of the next stage of chemical water and wastewater treatment could be a novel-hydrate coagulant (Zhao et al. 2011) with the ability to remove SS and P with very low dosages, resulting in less sludge amounts with the ability for nutrient recovery and inorganic metal recovery as a coagulant (Babatunde and Zhao 2007).

### 1.3 Understanding of phosphate removal during coagulation

Al and Fe salts (which are commonly called metal salts or Me salts) are conventionally considered as coagulants for P removal. The current understanding on the coagulation mechanisms of P removal by using of metal salts leads to the direct formation of insoluble  $\text{MePO}_4$  and Me-hydroxo-phosphate complexes. The other mechanism is adsorption of  $\text{PO}_4$  ions on to the particulate hydrolysis products, including the metal-hydroxide.

The stoichiometry of the  $\text{AlPO}_4$  formation indicates a molar ratio of 1:1 between  $\text{Al}^{3+}$  and  $\text{PO}_4^{3-}$ . However, in practice the ratios could be as high as 3:1 or even 5:1 in Norwegian WWTPs (Manamperuma and Ratnaweera 2014). The increased use can be partially explained by the consumption of the Me salts by hydrolysis reactions, which are competing with the phosphate reaction simultaneously (Ratnaweera 1992).

The efficiency of P removal is dependent on pH, concentrations of particles and P (Jiang and Graham 1998), temperature, types of coagulants, OH/Me ratio, z-potential, etc (Zouboulis et al. 2008). Among them, OH/Al ratio has been identified as one of the most important factors. Several published studies have shown that the higher the OH/Al ratio of coagulant, the higher the dose that is required for the removal of P (Fettig et al. 1990; Odegaard and Fettig 1990; Ratnaweera et al. 1992; Diamadopoulos and Vlachos 1996; Boisvert 1997; Zouboulis et al. 2008). Low OH/Al ratio coagulants hydroxide precipitation is favoured over P- precipitation as Al species are already polymerized before they are added to the water, resulting in increased efficiency of particle removal but decrease in P-

precipitation (Fettig et al. 1990). Furthermore, at low ratios, phosphates are removed dominantly by formation of Me-hydroxo-P-complexes, while at higher OH/Al ratios removal is made by  $\text{Me(OH)}_x\text{-P}$ . Me-hydroxo-P-complexes have higher capacity of phosphate removal than  $\text{Me(OH)}_x\text{-P}$  (Manamperuma et al. 2016).

A number of studies have pointed out that  $\text{PO}_4$  adsorption on to coagulant floc is an important mechanism of  $\text{PO}_4$  removal for both Al and Fe(III) salts and/or their pre-hydrolyzed forms. Hatton and Simpson (1985) reported higher P removal levels with polyaluminium chloride (PAC) than  $\text{Al}_2(\text{SO}_4)_3$  even if the removal efficiency of Ortho-P with PAC and  $\text{Al}_2(\text{SO}_4)_3$  were similar for equivalent coagulant dosages (Yeoman et al. 1988). The superior performance of PAC was associated to the specific properties of PAC which could allow extra  $\text{PO}_4$  to be removed.

Jiang and Graham (1998) carried out a comparative performance study between  $\text{PO}_4$  removal with polyiron sulphate (PFX, OH/Fe(III) molar ratio of 0.37) and  $\text{FeSO}_4\text{Cl}$  and report that for 80%  $\text{PO}_4$  removal from soft and hard waters, the dosage of PFX was approximately 20% less than that of  $\text{FeSO}_4\text{Cl}$ .

Contrary to these studies, Ratnaweera (1992) reported weaker removal of phosphates with increasing OH/Al ratio. The phenomenon is explained by the fact that the hydrolysis reaction is favoured by prepolymerised (high OH/Al) coagulants, thus the portion of Me salts available for phosphate precipitation will be comparatively less. Another explanation for this apparent controversy could be explained by the fact that the observations referring to comparatively less efficient removal of P with coagulants with increasing OH/Al were based on constant coagulation pH values, while the other studies may have variable coagulation pH thus influencing the process.

In order to achieve better coagulation efficiency and floc characteristics, synthetic polymers have been used in combination with metal coagulants, typically polyacrylamide and poly DADMAC. Cationic polyelectrolytes in combination with inorganic coagulants are efficient in Total-P removal from conventional wastewater, while they remain not efficient in removing P when used alone (Chen & Luan 2010; Moussas and Zouboulis 2009; Wei et al. 2010). This is because the major phosphate removal path is via precipitation, and while polyelectrolytes can remove or improve the removal particles it cannot dissolve phosphates.

## 1.4 Role of phosphorus in plant growth

Phosphorus is an essential macro-element, required for plant nutrition. It participates in metabolic processes such as photosynthesis, energy transfer and synthesis and breakdown of carbohydrates (Rivaie and Loganathan 2010; Achat et al. 2014). Phosphorus is found in the soil in organic compounds and in minerals. Nevertheless, the amount of readily available phosphorus is very low compared with the total amount of phosphorus in the soil. Therefore, in many cases phosphorus fertilizers should be applied in order to meet plant requirements (Mackay et al. 1984; Rivaie and Loganathan 2010). Phosphorus is found in soils both in an organic form and mineral form and its solubility in soil is low. Plants can only take up phosphorus dissolved in the soil solution, and since most of the soil phosphorus exists in stable chemical compounds, only a small amount of phosphorus is available to the plant at any given time (Achat et al. 2014).

The types of phosphorus compounds that exist in the soil are mostly determined by soil pH and by the type and amount of minerals in the soil. Mineral compounds of phosphorus usually contain aluminium, iron, manganese and calcium. In acidic soils phosphorus tends to react with aluminium, iron and manganese, while in alkaline soils the dominant fixation is with calcium. The optimal pH range for maximum phosphorus availability is 6.0-7.0 (Rivaie and Loganathan 2010).

In many soils, decomposition of organic material and crop residue contributes to available phosphorus in the soil. Plants take up phosphorus from the soil solution as orthophosphate ion: either  $\text{PO}_4^{3-}$  or  $\text{H}_2\text{PO}_4^-$  (Kvarnström et al. 2004; Hogan 2001; Morel 2000). The proportion in which these two forms are absorbed is determined by the soil pH, where at higher soil pH more  $\text{PO}_4^{3-}$  is taken up (Quin and Zaman 1958). The mobility of phosphorus in soil is very limited, therefore plant roots are only able to take up phosphorus from their immediate surroundings.

Wastewater sludge have been used for many years as sources of phosphorus for agricultural crops. Application to land is the preferred route for sludge producers as it offers beneficial recycling and the scope for reduced fertiliser inputs. Reducing effluent P concentrations concentrates phosphorus in the sludge and application to land is the simplest method of disposal, although the phosphorus can be of varying concentration and availability to plants (Brett 1997). Some sludge show poor nutrient availability despite their relatively high phosphorus content by analysis. There is a lack of information about the proportion of sludge phosphorus that can be used by plants, and the long-term effects of sludge deposition (Bertilsson 1997; Hogan and Morton 2001).

Application to agricultural land is likely to remain an important route for sludge management in the foreseeable future. It is therefore essential to deliver the farmers value for the efficient utilisation of nutrients in sludge applied to soil for agricultural production.

### 1.5 Role of coagulants on plant availability of phosphorus in the sludge.

Several researchers have studied the use of sludge as fertilizer. When compared with commercially available fertilizers and sludge from biological treatment, the level of plant availability of phosphorus (PAP) in coagulated sludge is disputed. Although early research (Watanabe et al. 2000; Sylvestris & Forests 2002; Gestring et al. 1982; Mengel 1982; Coker 1986) have not found any significant difference among these sludge types, some recent research has shown that it may be as low as 10% - 24% (Krogstad et al. 2010). Furthermore, behaviour of coagulated sludge and PAP are strongly dependent on the nature of the OH/Al ratio, phosphate concentration of wastewater, physico-chemical properties and plant species (Hylander 2001). Continuous use of aluminium/iron contaminated sludge may lead to an increase in aluminium/iron bioavailability or change in their fractionation of soil with time due to their less soluble forms initially present in sludge (McBride 2003). Subsequently, the reduction of metal (aluminium or iron) in sludge will increase the PAP.

Hanserud (2015) explored the theoretical potential of wastewater sludge to supply the P fertilizer requirement of crops in Norway. It was found that if sludge to be well redistributed within Norway, the whole country could be self-sufficient in P fertilizer for all crops assessed in both in the short and the long term.

In Norway, more than 70% of wastewater is treated using coagulation as a unit process and over 85 % of wastewater sludge is used in agriculture (Berge and Mellem 2011). Toxicity of metal salts in plant growth is reported in the literature, which could be a threat to the use of sludge in agriculture. Zhang and Zhou (2005) documented that the ecotoxicological effects of aluminium-based coagulants are of concern because of the toxic effects on vegetables. The results shows that root elongation of the vegetables is a more sensitive indicator than seed germination for evaluating the toxicity of Al. As a single influencing factor, H<sup>+</sup> has no significant direct effects on root elongation under acidic experimental conditions. The toxicity of Al plays the main role in inhibiting root elongation and seed germination and strongly relates to changes in pH. There is a markedly positive relationship between the inhibitory rate of root elongation, seed germination, and the concentration of Al at pH 4.00 (p < 0.01). Undoubtedly, the Al toxicity caused by Al-based coagulants at a neutral pH is relevant when

treatment solids are used in agriculture (Zhang and Zhou 2005; Yang et al. 2010). The toxicity of Al based coagulated wastewater sludge used in agriculture must be studied.

The use of sludge from the coagulation process as a fertilizer could be a challenge if a good part of phosphorous is not easily available for plants. Thus, the farmers who are not willing to pay for sludge today, may be just as reluctant to accept even free sludge in the future if PAP is not in the acceptable range for farming. That is why it is important to improve PAP and consequently increase the value of coagulated sludge.

Many research works focus on improving sludge quality in order to make nutrients in WW available for plants. The most widespread approach is to treat sludge and transform binded phosphorus into available form. So the sludge after several steps of post-treatment could have a higher PAP. The methods based on such approaches are digestion, high temperature pyrolysis or chemical treatment of sludge (Hossain et al. 2011; Hargreaves & Rupasinghe 2008). This requires significant energy consumption and the need for additional equipment.

Plant growth studies have indicated that the content of aluminium or iron in sludge is inversely proportional to the phosphorus uptake by plants (Øgaard 2013). Hence, a conclusion is drawn that reduction of aluminium or iron in sludge will increase the PAP.

## 1.6 Quantification of Plant Availability of Phosphorus

Several approaches to quantify PAP is reported in the literature. A soil phosphorus test involves phosphorus extraction from soils followed by a quantification of the nutrient in the extracted solution. The most widely used soil phosphorus tests are chemical extractions, such as Bray 1 & 2, Olsen, Mehlich I & III methods (Mehlich 1984). Those chemical extractions are not applicable over all soil types, which is a limitation for soil phosphorus extraction. The ion-sink extractions, including ionic exchange resin membranes, resin bags, FeO coated filter papers or strips, simulate plant roots to extract phosphorus from soils without alteration of soil characteristics and have the advantage of extracting phosphorus from a variety of soil type regardless of soil properties (Nutrition and Veterinary 1978; Schoenau & Huang 1991; Chardon and Chien 1996; Myers et al. 2005). The main phosphorus determination is the use of colorimetric procedures, by Murphy and Riley (1962) (Murphy & Riley 1962). Inductively Coupled Plasma spectrophotometry is becoming more popular for multi-element determination. The isotopic dilution ( $^{32}\text{P}$ ) techniques, the  $^{31}\text{P}$  Nuclear Magnetic

Resonance solution and the synchrotron-based techniques can provide insights into phosphorus chemistry and forms in soil and residual materials (Zheng et al. 2000).

They used the ammonium lactate extractable phosphorus method, an extraction method which was commonly used to measure PAP in Nordic soils (P-AL)(Kvarnström et al. 2004). Soil weighing 5 g is extracted with 100 ml of a 0.1M ammonium lactate and 0.4M acetic acid solution for 90 min (Schick et al. 2013). To analyse Total-P the gross and net transfers of phosphorus ions between solution and substrate in suspensions is measured. Kvarnström et al. (2004) controlled several physico-chemical mechanisms such as adsorption, precipitation/dissolution, and diffusion caused by surface heterogeneity and porosity, as well as biological mechanisms such as mineralization of organic compounds containing phosphorus to measure transfer of phosphorus ions between the solid and liquid process. Morel (2000) used two experimental approaches those have been mainly developed to evaluate and describe the dynamic of transfer solid and liquid. One is a sorption experiment that provides information on the net transfer of phosphorus ions from solution to substrate after adding increasing phosphorus rates. The other consists of labelling phosphorus ions in solution with radioactive phosphorus isotopes Kvarnström et al. (2004) used  $^{32}\text{P}$  and to simultaneously analyse the kinetics of isotopic dilution and phosphorus ions concentrations in solution at steady state. Net transfer, i.e. the added phosphorus that is adsorbed on substrates, was determined after 40 h of reactions. At this sorption state, the gross transfer of phosphorus ions was determined as a function of solution phosphorus concentration and time. The isotopic dilution procedure was used to analyse the ability of phosphorus on substrate, i.e. native plus accumulated phosphorus as well as added phosphorus that was adsorbed (Zheng et al. 2000; Kvarnström et al. 2004).

Øgaard (2013) carried out growth experiments with rye grass in 12 different types of sludge in pots over six months with monthly harvesting and growth analysis. Control samples were evaluated and all pots were supplied with necessary minerals to minimize the influence of external factors. The results showed a decrease of P-uptake (mg-P/pot) from 32 to 22 when the Total-Al content was increased from 0.3 mmole/kg sludge to 4.0 mmole/kg sludge. Thus, the results suggested an inverted proportionality between the PAP and aluminium content.

## 1.7 Coagulant dosing control systems (CDCS).

Optimization of the coagulation process is important to the full treatment process, particularly from an economical point of view relating to coagulant and sludge treatment costs during daily operation in a treatment plant. Poor dosing control leads to excess use of

expensive chemicals, failure to meet the water quality requirements, increased sludge production, decreased sludge value and reduced efficiency of subsequent treatment processes. On the other hand, efficient dosing control systems may reduce the labour costs, chemical costs and improve compliance with treated water quality targets.

The reviews on coagulant dosing control systems were provided by Dental (1991), Ratnaweera (2004) and Ratnaweera and Fettig (2015). Most chemical water and WWTP are adapted to use at least a flow proportional coagulant dosing control system (Dental 1991). A survey in 2004 showed that more than 80% of drinking water treatment plants (DWTP) and 83% of WWTP use a flow proportional dosing control system, and sometimes in combination with pH overdrive systems (Ratnaweera 2004). Literature reviews show that despite several recently commenced and ongoing research works, not much has changed in the field of full scale dosing control applications (Ratnaweera and Fettig 2015). Most plants still use dosing control systems with one or two water quality parameters, which could be providing results far away from the optimal dosage.

Beside the pH and flow proportional traditional coagulant dosing control systems (CDCS), researchers have started using other physical sensors such as turbidity and UV absorbance as parameters in CDCS for drinking water treatment (Ratnaweera and Fettig 2015). For example, a successful control strategy was developed with an equation containing nine empirical constants by evaluating four years turbidity, conductivity and temperature data (Jackson and Tomlinson 1986). Hernebring (1987) developed a simple empirical equation for predicting ALS dose based on natural organic matter (NOM) concentration measured by UV absorbance (Hernebring 1987). Another UV absorbance concept was developed by Edzwald (1993); characterizing the properties of NOM with coagulant dosage (Edzwald 1993). An empirical correlation between pH, initial NOM and residual NOM concentrations on coagulant demand was suggested by Eikebrokk and Fettig (1990).

In WW treatment effluent Ortho-P is used as an additional parameter, but not used in feed-back automatic CDCS (Storhaug 2009). Furthermore, feed-forward control of treated water quality is not used for automatic CDCS (Ratnaweera and Fettig 2015). Tik and Vanrolleghem (2012) proposed a CDCS scheme by using turbidity after the primary sedimentation.

Thomas et al. (1999) presented an overview of attempts to model the floc formation process mathematically. Nevertheless, there are no real-time usage examples in CDCS.

A number of studies in order to develop relationship between several inputs and one output parameters by mathematical tools have been started in recent years. Lu et al. (2004)



and Rathnaweera (2010) developed multiple models, a novel real-time water quality parameter based CDCS by partial least squares regression (PLSR). AlGhazzawi and Lennox (2009) gave a comprehensive overview of the use of principal component analysis (PCA) and partial least squares (PLS) statistical process control methods. They developed a model predictive control condition monitoring tool that enables users to detect abnormal controller operation and resolve abnormalities when necessary, but they also point out that process knowledge and experience are necessary to analyse model predictive control or process abnormalities correctly. Trinh and Kang (2011) developed a quadratic model studying the relationship between dosage and pH as inlet parameters and turbidity and dissolved organic carbon (DOC) removal as response parameters. Results show that there is a very small pH range for achieving both removal efficiencies while the pH range remains wide for one parameter. A two-level fractional factorial design method was applied with minimum dosage required and the residual turbidity after settling.

Furthermore, use of Artificial Neural Network (ANN) in water and WW technology for CDCS have increased in recent years. Zhang & Stanley (1999) and Baxter (1999) developed ANN models for NOM removal. They reported a successful evaluation of ANN in a pilot scale plant and the models can help to reduce coagulant costs. Valentin (2001) suggested a coagulation control system based on unsupervised and supervised neural network models that demonstrate how process data can be used to develop and train a feed-forward controller in the form of a neural network to accurately predict a suitable coagulant dose. Yu (2000) studied the use of raw water pH, conductivity, turbidity, and effluent turbidity on optimal coagulant dosage in an ANN model. Maier (2004) built two multilayer perceptron (MLP) neural network models, where the first model uses raw water pH, turbidity, conductivity, UV, DOC, alkalinity and Al dose to predict residual turbidity, colour and UV absorbance. The second model, uses raw water parameters and describe treated water quality for prediction of optimal dosage, final pH and residual Al concentration. Zhang and Luo (2004) built MLP with raw water temperature, pH and turbidity as inputs and coagulant dose and SC as outputs. Lamrini (2005) reported an ANN model with four years of data of temperature, pH conductivity, turbidity and Dissolved oxygen (DO) as input parameters. Hernandez (2006) used the same ANN model based on the concept where the information generated was integrated into plant operation as input to a diagnosis system. Wu and Lo (2008) and Han (1997) compared ANN and adaptive network based fuzzy interference system (ANFIS) models and concluded that the ANN model is better. The same researchers in 2010 improved the model's predictive capabilities. The ANFIS-based model for real-time dosing

control was developed by Kumar (2013) trained with jar-test data and compared with ANN and applied in pilot plant. Dellana and West (2009) compared a linear autoregressive integrated moving average model and a time delay neural network model for Biochemical oxygen demand (BOD), nitrogen and P removal. Zheng (2011) developed a radial basis function neural network model with pH, coagulant dose, P/Al ratio and agitation speed as input parameters and Chemical Oxygen Demand (COD) removal as output.

In recent years, fuzzy logic controllers have become popular in process control. The approach by Liu & Huang (1997) was a fuzzy logic controller (FLC) with a Streaming Current Detector (SCD) utilized in the automatic control of the coagulation reaction. pH and streaming current are used as control process outputs, and coagulant dose and base dose are chosen as control process inputs. They are monitored on-line and transduced through a FLC, while ‘turbidity in and out’ are the FLC set point parameters. Results show that this combination functions to a satisfactory level for coagulation control. Heddam (2012) developed grid partition-based and subtractive clustering-based ANFIS models for a feed-forward network, where adaptive learning parameters are used to achieve optimal output data. Chen and Hou (2006) developed a fuzzy control model for drinking water with four years of effluent pH and turbidity data. Wan (2010) developed a neural-fuzzy process controller with input of flow, COD and coagulant dose and defined effluent COD.

Unlike many other industrial processes, coagulant dosing is difficult to control using feedback concepts, primarily due to the 1–6 hours of sedimentation time and the rapid influent quality fluctuations during that period. On the other hand, there is no simple method to determine the optimal coagulant dosage to maintain effluent quality levels (for example Total-P) with influent quality fluctuations and sedimentation times. This situation forces most treatment plants to run with an overdose, which results in many adverse effects, including the reduction in PAP.

Feed-forward based dosing control systems are used in some WWTPs. In most cases they are limited to flow or flow proportional systems as noted earlier. DOSCON AS of Norway has developed a dosing control system based on multiparameter surveillance, with successful results (Ratnaweera and Fettig 2015).

## 2 Research hypothesis, objectives and rationale

### 2.1 Research hypothesis

As presented in the previous chapter, phosphates are critically important in agriculture while mineral phosphates are depleting rapidly. Therefore, it is necessary to use phosphates in wastewater and wastewater sludge. While wastewater sludge is already used in agriculture, some researchers have reported a significantly reduced availability of phosphates for plants (PAP) when coagulated. Since over 70% of wastewater in Norway is treated either chemically or chemically-biologically and over 80% of sludge is used in agriculture, this creates a serious uncertainty of the current practice.

Research indicates that the PAP is inversely proportional to the Al and Fe content in sludge. Thus, one important solution to increasing PAP is to reduce the Al or Fe content in sludge, i.e. use less in coagulation, without reducing the treatment efficiencies. Avoiding unnecessary over-dosage due to inaccurate estimation of the optimal dosages should contribute to the improvement of PAP. The first hypothesis is that it is achievable with a proper dosing control system (ADCS). However, further reduction of metal salts may be required. The use of cationic polymers to remove particles while only using metal coagulants for the phosphates could drastically reduce the metal salts consumption, which is the second hypothesis. Both hypotheses provide a solution to the increase PAP in coagulated sludge, thereby resolving a critical challenge that the industry may face.

However, if any of the above two hypotheses are experimentally or analytically disprove, it is critically important to have an insight to the underlying mechanisms, so new hypotheses and solutions to improve PAP can be launched.

## 2.2 Research goal and objectives

The overall goal of this research work is to increase the PAP in coagulated sludge, elaborating the possibilities to reduce the inorganic coagulant usage by improved dosing control and by partial substitution of inorganic coagulants with cationic polymers without jeopardising the treatment efficiencies.

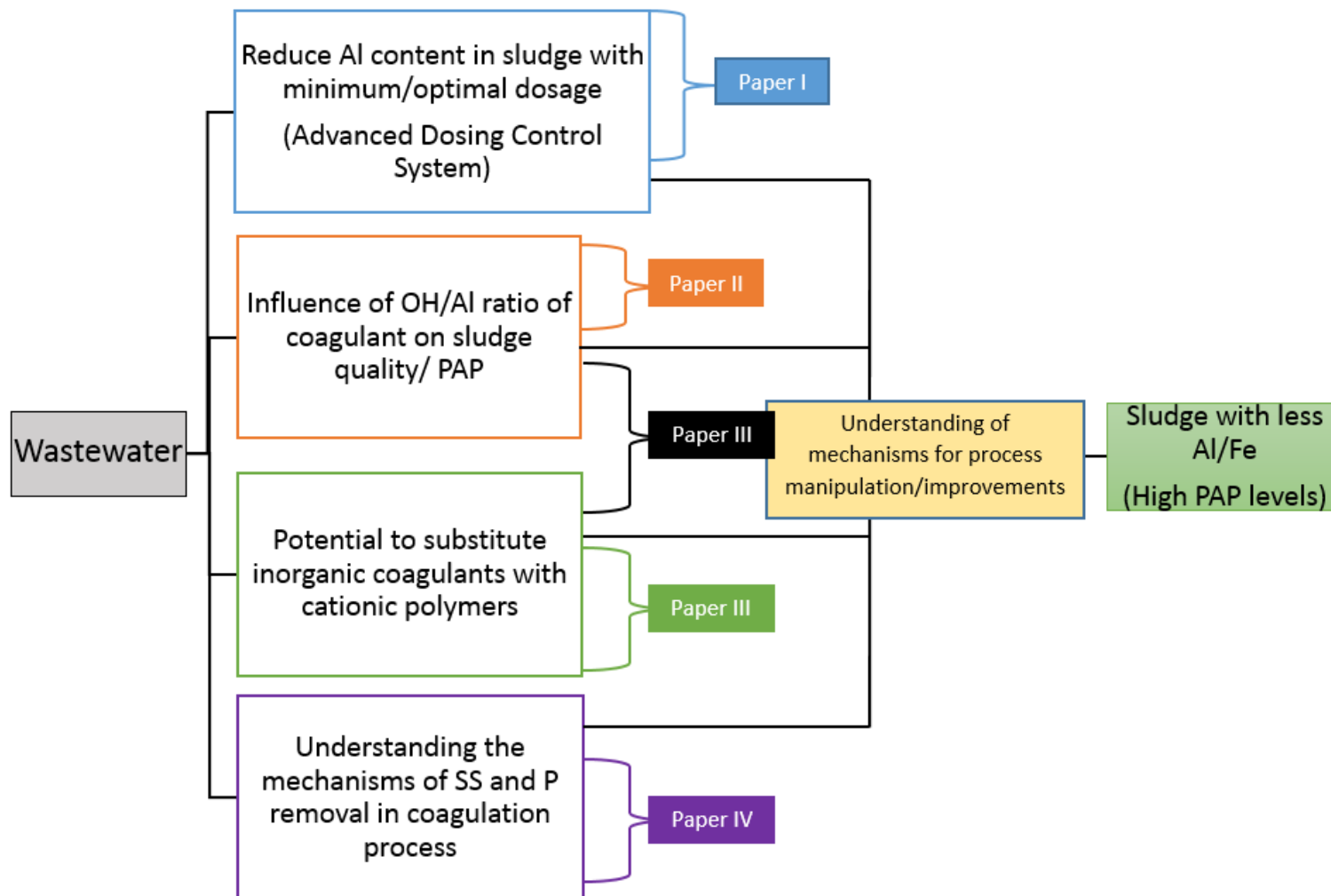
The specific objectives were to:

1. Validate the flexibility of an advanced dosing control system by (feedback control) including required effluent water quality parameters (**Paper I**)
2. Evaluate the influence of OH/Me ratio of inorganic coagulants on PAP levels in coagulated sludge (**Paper II**)
3. Evaluate the possibility of partially substituting inorganic coagulant with cationic polymer to improve PAP in sludge (**Paper III**)
4. Understanding the mechanisms of SS and P removal in the coagulation process (**Paper IV**)

The conceptual framework of the thesis is presented in figure 2.

## 2.3 Rationale

The overall rationale for the work presented in this thesis is to provide a better understanding of the underlying factors involved in optimizing coagulant dosage to obtain (valuable) readily usable coagulated sludge with high PAP as an eco-friendly product. A better understanding of these underlying factors could improve current global issues of eutrophication that are caused by untreated/poorly treated wastewater, and provide alternative sources of phosphates for agriculture, considering the depleting global mineral phosphate reserves.



*Figure 2. Conceptual framework of the PhD thesis.*

Despite that most WWTPs report satisfactory treatment results with regards to SS and P removals, the Al:P molar ratios applied indicates a significant over-dosage of inorganic coagulants. This is caused by the inability to define the optimal dosages using today's common dosing strategies, which are based on flow proportional dosing, at best with pH overriding. DOSCON AS, Norway, has developed a multiple-parameter and multiple-model based advanced coagulant dosing control system (ADCS) that will be used in this research to elaborate the possibilities to reduce inorganic coagulant consumption to increase PAP. The ADCS estimates the optimum coagulant dosage based on real time measurement of different water quality parameters. One of the main aims of improving the ADCS DOSCON is to be flexible to reduce or increase the treatment efficiency of any required effluent water quality parameter. Accurate, optimal dosage will ensure good and even treatment efficiencies at the lowest possible coagulant dosages, giving least chemical costs and minimum sludge productions. Thus, defining the optimal coagulant dosing at all times is critically important. An ADCS concept of this kind was evaluated in a full scale WWTP, as addressed in **Paper I**. Existing models of the dosing control system re-calibrated because, treatment plants with bypass lines are required in discharge permits to include the discharge loads of total flows. Thus, the plants are evaluating if the treatment efficiencies can be increased to even higher levels during normal operational times to maintain the annual averages at required levels. The dosing control system is designed to predict optimal coagulant dosage for normal operational days. The system is then calibrated to increase the treatment efficiencies while also rapidly increasing the flow rates. The system proves to function well until it reaches limitations related to the capacities of the particle separation process.

One of the biggest challenges in coagulation is handling the coagulated sludge. Almost all aluminium and iron added during the coagulation process are transferred to the sludge phase. Wastewater sludge is no longer treated as a waste, but as a resource, and now it is commonly considered as a valuable component in agriculture. There are two main research groups arguing the fate and value of coagulated phosphates in agriculture: The first group argues that the PAP is significantly reduced in chemically treated sludge, independently of the chemical form (Krogstad et al. 2005). The second group argues that phosphates are normally found as aluminium phosphates, iron phosphates or calcium phosphates. It is argued that where iron phosphates are more difficult for plants to use, phosphates in aluminium phosphates and calcium phosphates forms may be more easily available for plants (Reijnders 2014). However, sludge with less PAP has its own advantages such as slow release of P over the years without being washed out too fast. **Paper II** evaluates the PAP levels of sludge with

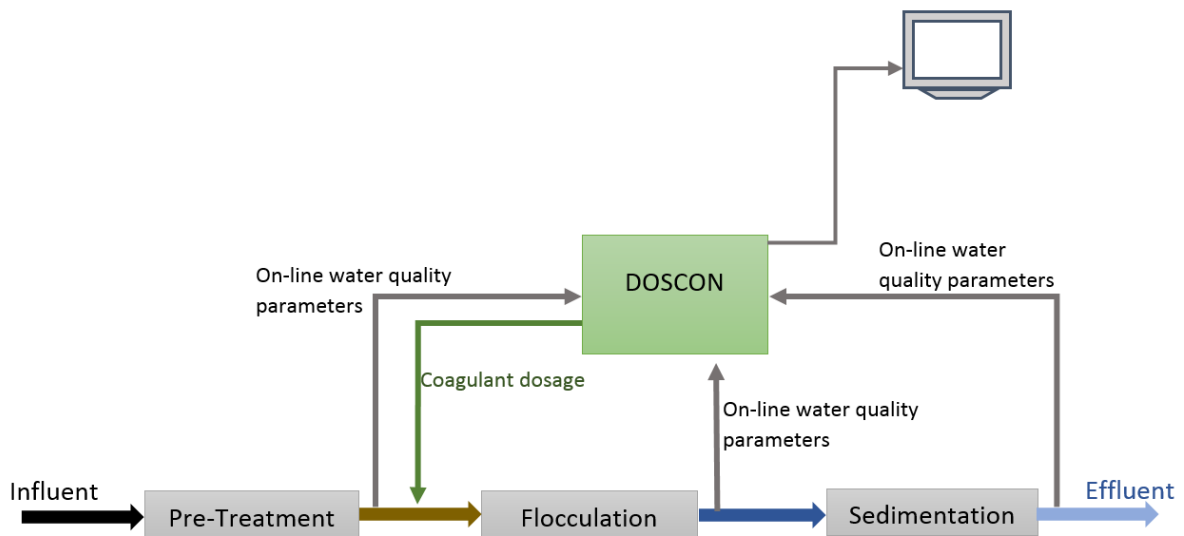
experiments and document that PAP levels are lower in coagulated sludge. Coagulants with different OH/Al ratios are used to compare PAP levels of coagulated sludge.

A possible way to reduce inorganic metal in coagulated sludge is to substitute inorganic coagulants with cationic polymers. Assume that the SS and particulate P will be removed by cationic polymers as particles, and dissolved P by precipitation with inorganic coagulants. The amount of metal coagulant required for particle removal is found to be reduced and as a result metal content in sludge decreased and PAP increased. **Paper III** discusses obtained results and possible mechanisms of SS and P removal during the coagulation process. During the combined coagulation, substitution possibilities up to 44% were observed with low coagulant-to-particle ratio. The predominance or significance of the adsorption-charge neutralisation (ACN) is assumed in this case. When there is much Al-species compared with the amount of particles (for i.e. water with low concentrations), the sweep-floc mechanism is favoured. Then the cationic polymers have less possibility to compete and substitute aluminium.

When most of the particles be removed by cationic polymers, the molar ratio of Al:P in pre-treated (particle free) wastewater becomes closer to 1:1. Thus, a reduction of metal coagulants of about 70-75% of metal coagulant reduction by substituting inorganic coagulant by cationic polymer should be anticipated, referring to the change in molar ratios from 3:1 to 1:1. However, the results show only a 44% reduction. The influence of particle concentration on the P removal is complex and cannot be completely explained only by coagulation. Other contaminations in the water may interfere with coagulants, both chemically and physically. Particles are predominantly removed by charge neutralization - precipitation and sweep floc mechanisms, while P is removed by the precipitation mechanism of metal- hydroxo - phosphates complexes and direct adsorption in the coagulation process. **Paper IV** addresses simultaneous particle destabilization and P precipitation by coagulants with different particles to P concentrations and OH/Al ratio of coagulant.

### 3 Experimental procedures and methods

Automatic Advanced Dosing Control System (ADCS) is a concept to increase water treatment efficiencies by optimising coagulant dosage. Optimal coagulant dosage strongly depends on various parameters in the water treatment process. Most of these parameters vary rapidly and non-proportional to each other during the day, as they depend on internal activities of industry, weather, human activities and on various incidents, which are sometimes unpredictable. Achieving an optimal coagulant dosage based on incoming flow- or time-proportional dosing is therefore impossible. ADCS estimates the optimal coagulant dosage based on real time measurement of different water quality parameters, as illustrated in Figure 3. On-line water quality instruments send real-time values to the SCADA system. After validation of measurements and estimation of non-validated measurements, ADCS calculates the optimal coagulant dosage and sends a dosing signal to SCADA or the pump. Calculation and prediction of optimal coagulant demand is based on chemometrics and intelligent logic control technologies (DOSCON, 2011).



**Figure 3.** Schematic diagram of ADCS concept after DOSCON.

The domestic wastewater used in this thesis were taken from two WWTPs. The NRA WWTP (NRA) has a capacity of 130 000pe and 55 000m<sup>3</sup>/day. It is located in Lillestrøm, Norway and built inside a tunnel of rock that serves the population of the four municipalities Nittedal, Lørenskog, Rælingen and Skedsmo. The NRA consists of four unit processes: The pre-treatment process consists of grit chambers, sand and grease traps and pre sedimentation;



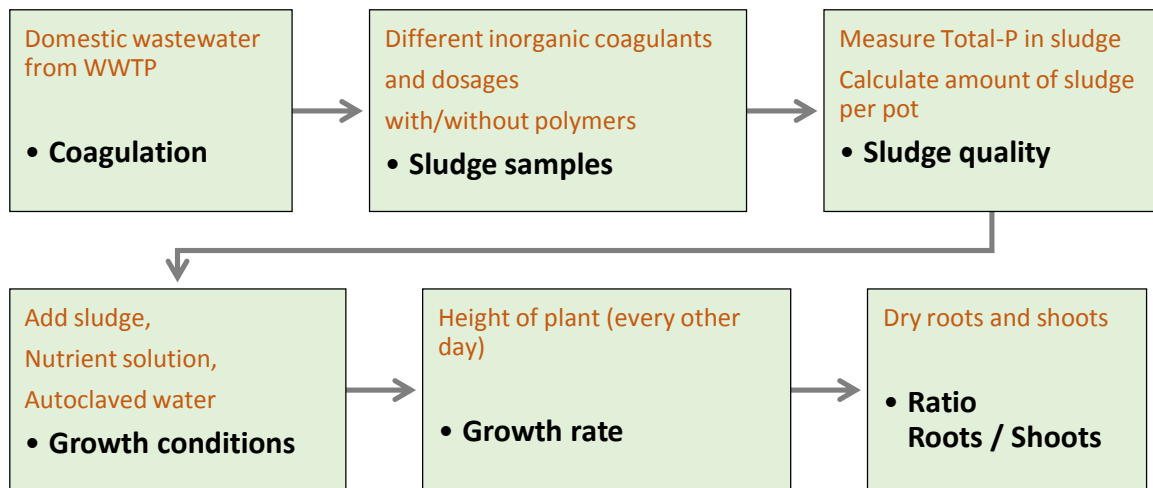
biological process with a series of moving bed biofilm reactors; chemical coagulation process; sludge from all unit processes is mixed together and treated in a sludge treatment process. The sludge is distributed to farmers and green areas after dewatering, thickening and stabilization. Rathnaweera (2010) documented a hydraulic retention time of the post sedimentation tank of about two hours.

The Skiphelle WWTP (SWWTP) is built as a mechanical and chemical precipitation plant in Drøbak, Norway. SWWTP consists of three processes: Mechanical pre-treatment; chemical coagulation stage and sludge treatment. The dewatered and stabilised sludge is distributed to farmers, green areas or landfills. The treated water is released to the Oslo fjord.

All experiments in this work have two sets of results. The first set is data collection and full-scale evaluation studies of ACDS performances held at NRA. The second set is jar-test coagulation experiments with synthetic wastewater and wastewater from NRA and from SWWTP. The compositions of standard synthetic wastewater are given in the subsequent chapter and were adjusted to required levels by phosphorus and SS contents. Some experiments were carried out randomly with domestic wastewater from NRA and DWWTP.

### 3.1 Growth experimental setup

To evaluate the PAP in realistic conditions, it is necessary to carry out growth tests using either pots or hydroponic systems. Wheat seeds in hydroponic pots were set up in a temperature, humidity and light controlled greenhouse. The experiment was set up using a random design with three replicates of each sludge sample, resulting in a total of 36 hydroponic boxes. The experiment consisted of eight treatments: two dosages of two coagulants Aluminium Sulphate (ALS) and Polyaluminium Chloride (PAX-18) in two initial Ortho-P concentrations. At the start, 2 g of Watman filter papers were measured into each 600ml plastic box (10 cm X 10 cm X 6 cm) and a calculated amount of sludge was added to each box. One gram of wheat seed and the same amount of nutrient solution were placed in the each box and autoclaved water was added to each box until the weight of the box reach the desired level.



*Figure 4. Schematic diagram of plant growth experimental setup*

### 3.1.1 Planting and harvesting

Each box was sown with 1 gram seeds of spring wheat (*Triticum aestivum*, cv. Vinjett) on the filter paper. After sowing, all boxes were placed on trolleys in a greenhouse at NMBU to simulate Norwegian summer climate (14 h day, 10 h night, 20 °C day-time, 16 °C night-time, air humidity 70% and light intensity 24 $\mu$ mol). During growth and until harvest, the moisture content was checked by weighing each box every second day and, when needed, adjusted with autoclaved water. At watering, the position of trolleys in the room was systematically shifted.

Harvest was performed 12 days after planting and the straw and root fractions were prepared and weighed separately. Biomass weight was determined after cutting the biomass fractions into small pieces and drying them at 110 °C for three days. In addition to absolute biomass fractions, relative biomass fractions, i.e. the shoot and root biomass divided by the total biomass, were calculated.

### 3.2 Data collection and full scale evaluation

NRA used an ADCS system provided by DOSCON AS, Norway since 2009 and reported good effluent qualities resulting in more than 94% Total-P removal, 91% of COD and 80% of total nitrogen removals (VA Support, 2012). The coagulant usage was reduced by over 30% and the molar ratio of Al:P was reduced from 2.5:1 to 1.8:1 after the installation of DOSCON, according to performance statistics (VA Support, 2012). The overall effluent quality was not a challenge at this WWTP. However, the new discharge permit required 94% of Total-P removal including the by-pass, thus NRA decided to increase the maximum flow

through the plant from 700 L/s to 1300 L/s. It has been a challenge to the ACDS to secure equally good treatment efficiency while keeping the coagulant usage at a minimum. The system improvement of ACDS was carried out to face these challenges.

### 3.3 Coagulation experiments with model wastewater

The experiments carried out with model wastewaters. Compositions of synthetic wastewaters differed by phosphorus and suspended solids contents. The exact compositions of model wastewaters are given in Table 1.

**Table 1.** Composition of synthetic wastewater (Ratnaweera 1991)

mg/l	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10	Type 11	Type 12
CaCl <sub>2</sub>	255	255	255	255	255	255	0	0	0	255	255	255
NaHCO <sub>3</sub>	400	400	400	400	400	400	0	0	0	400	400	400
NH <sub>4</sub> Cl	200	200	200	100	100	50	0	0	0	200	100	50
K <sub>2</sub> HPO <sub>4</sub>	30	15	4.5	15	25	25	10	20	30	0	0	0
Humic	10	10	10	5	5	2.5	0	0	0	10	5	2.5
Milk	600	600	600	300	300	100	0	0	0	0	0	0
Starch	120	120	120	60	60	30	0	0	0	0	0	0
Latex	20	20	20	10	10	5	0	0	0	20	10	5
Bentonite	160	160	160	80	80	40	0	0	0	160	80	40

The chemicals used were coagulants from Kemira ALS (Aluminium Sulphate), PAX-18 (Polyaluminium Chloride), and PAX-XL-61 (prepolymerised Polyaluminium chloride), with OH/Al ratios of 0, 1.1 and 1.9, respectively. Five dosages of each coagulant was used, including both under- and over dosages than optimal dosage. The optimum doses were determined in the preliminary experiments. Two types of polyacrylamides from SNF-FO 4350 and SNF-FO 4240 were chosen as organic cationic polymers and 1 g/l solutions of polymers were used. For each of the polymers, dosages of 1 mg/l, 3 mg/l and 5 mg/l were used.

The coagulation experiments were carried out at coagulation pH values (6.0 ±0.2) and (7.5±0.2). For the coagulation process to result in the desired pH value, the initial pH of raw water was adjusted depending on the coagulant dosages added.

For the coagulation experiments the jar-test apparatus (Kemira Flocculator 2000) with six beakers was used. The mode of mixing was; rapid mixing of 400 rpm for 30 seconds, then slow mixing of 60 rpm for 10 min followed by sedimentation for 20 min.

Two types of dosing modes were used in the experiments; simultaneous and sequential dosing of polymer and coagulant. During the simultaneous dosing, coagulant and organic polymer were added simultaneously to the jars at the beginning of rapid mixing. In the sequential dosing, the sample was first coagulated with polymer alone and then the supernatant was separated and coagulated again with inorganic coagulant. After sedimentation, we collected about 200 ml of supernatant and used it as a sample for further analysis.

We analysed SS, Total-P, Ortho-P and turbidity in the collected samples. Determination of SS content was done at constant pressure filtration followed by drying 105<sup>0</sup> C for 2 hours. Total-P and Ortho-P contents were measured according to ISO 6867/2004. Turbidity was measured using a Hach 2100Q portable turbidimeter. The extents of SS removal and Total-P removal were the main parameters by which the evaluation of treatment efficiency was done.

The second set of experiments were carried out with six model wastewaters, which had variable concentrations of SS and phosphates. Sludge or precipitant obtained after coagulation were analyzed for bonds of the coagulant-suspended solids and coagulant-phosphates. To obtain sludge from SS = 0 waters, Total-P concentrations of 10, 20 and 30 mg /P l were used with Al dosages of 40 and 50 mg Al/l. Similarly, to obtain sludge without Total-P, model wastewater was prepared without phosphates with respective coagulant dosages.

In order to reduce the number of required experiments while retaining the most important features, we made a fractional factorial design of the experiment using the UNSCRAMBLER<sup>®</sup> X 10.3 program.

### 3.4 Plant growth experiments with real wastewater

Experiments were carried out in the laboratory with wastewater from SWWTP. Coagulation experiments were carried out as explained above in section 3.3. The same coagulants, polymers and the combine dosing methods were used and obtained sludge was collected for growth experiments.

The initial concentration of wastewater was adjusted to 3.36 (low) and 6.18 (high) mg-P/l with addition of KH<sub>2</sub>PO<sub>4</sub> in order to get initial Total-P concentrations 4 and 8 mg-P/l, respectively.

Coagulated sludge is reported to be contaminated with almost all microorganisms found in wastewater (Tchobanoglous et al. 2003). Fungi have the strongest impact on plant growth, as under appropriate conditions some species can infect plants, while others can influence the route for plant nutrient uptake. Therefore, sludge samples were thermally treated in plant growth experiments. To eliminate populations of plant pathogens, the sludge was microwaved at 900 W heating power for 4 minutes. The preliminary experiments showed that at 900 W 4 minutes was the minimum required time for elimination of pathogens. Additionally, content of Total-P and Ortho-P in all sludge samples and in selected sludge samples were analysed.

Analysis were carried out using Hach Lange CLK349 and Hach Lange Aluminium-Method 8012-Powder Pillows Rapid Tests. A Hach DR 3900 spectrophotometer together with Hach LT 200 heating block was used. Randomly selected samples were analysed in several replicates to control accuracy and to reduce the analytical errors.

To compare the growth rates of plants, all the nutrients including P were provided equally in each pot. Based on Total-P in coagulated sludge, the amount of Total-P was calculated as 3 mg per pot. Parallel control pot samples were prepared with full nutrients including P, without P and without supplementary of any nutrient (which were supplied only by water).

As nutrient solution, a composition of N:P:K:Mg:Ca with ratios similar to standard commercial fertilizer content for greenhouse plant growth tests was chosen (Resh 2012). Pre-treated wheat seeds were used for growth tests, which were disinfected with 1% chlorine water and germinated in autoclaved water for 24 hours. The bottom of each pot was covered by Watman filter paper to prevent drain-off of sludge and nutrient solution. The same amount (grams) of germinated seeds and calculated amount of sludge were placed into the prepared pots. Conductivity of sludge-nutrient solution mixture in each pot was maintained between the levels of 1000 – 1100  $\mu\text{S}/\text{cm}$  by the addition of autoclaved water.

Hydroponic plant growth tests were carried out in greenhouse over 12 days and with 3 sets of replicates in each experiment, including control samples. Greenhouse standard conditions were daylight from 08:00 to 22:00 at temperature 20 °C, with the dark period from 22:00 to 8:00 at 16 °C. Autoclaved water was used for watering during the full period of experiment, and the growth rate of plants and biomass allocation (BA) were analyzed parameters. The mean value of biomass allocation of plants was estimated by mean mass of roots divided by mean mass of shoots.

Although the PAP can be evaluated using advanced analytical techniques reported in the previous chapter, we have used the simple estimation presented by Øgaard (2013), namely the PAP's inverted relationship with the content of aluminium and iron in sludge. Plant growth and BA were used to compare the PAP levels in the sludge and in control samples, together with the content of aluminium or iron salts.

## 4 Results and discussion

### 4.1 Flexibility of advanced dosing control system.

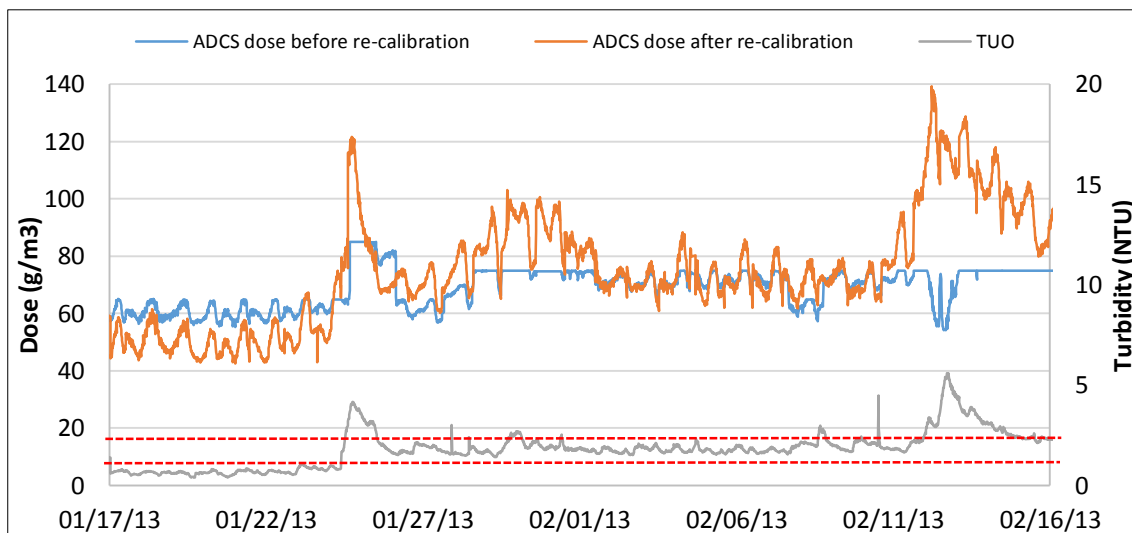
This section is related to **Objective 1**. Historically, the WWTPs were not constructed to treat all wastewater transported to the plant, and therefore accepted bypassing all or some of the process at extremely high inflows. Heavy rains and snow melting periods are typical such events, and the frequency and the amplitude is anticipated to be even higher in the future, due to the impact of climate changes. In such situations, bypasses are necessary both in the sewer networks and at the WWTPs. Authorities in some countries have now started to require total pollution discharge documentations, and some WWTPs in Norway already have or soon will get their discharge permits related to the total wastewater volumes received or discharged, rather than only for the portion that goes through the WWTP. In practice, this leads to significantly higher treatment requirements on the portions that go through the plant in order for the average discharges meet the requirements.

NRA has already received such a requirement, i.e. to remove 94% of Total-P in annual averages in the effluent including bypasses. Two strategies are suggested: (1) increase the amount of wastewater that goes through the plant from 700 L/s to 1300 L/s with treatment efficiencies of over 96%. (2) construct a simple mechanical/chemical treatment facility for all or parts of the bypass. The plant has the physical capacity to increase the flow as suggested, however, the coagulation – sedimentation stage is not readily capable of handling the increase. Although organic polymers will improve the settability, the securing of Total-P removal efficiencies at externally diluted water would not be possible with them. Thus the increase of dosing of inorganic coagulants seems to be inevitable. This will increase the aluminium content in the sludge and PAP will reduce.

The change of incoming flow could be quite fast and a less sophisticated dosing control system or a manual adjustment will either lead to poor treatment results or overdosing of coagulants.

The hypothesis in this case is that an ADCS should be able to manage such variations, increase of flow and variation of concentrations promptly and efficiently. Thus the tests were carried out at NRA to calibrate and evaluate ADCS performance under these conditions.

An analysis of the Total-P values in the inlet of NRA shows that it can vary between 2.0-6.0 mg-P/l. A 96% removal in this case corresponds to the outlet Total-P of 0.09- 0.25 mg-P/l. Since it is simpler to use the outlet turbidity as a surveillance parameter, it was estimated that an outlet turbidity of 2-3 NTU would satisfy the requirement of the average Total-P removal >96%.



**Figure 5.** Response of ADCS to effluent turbidity

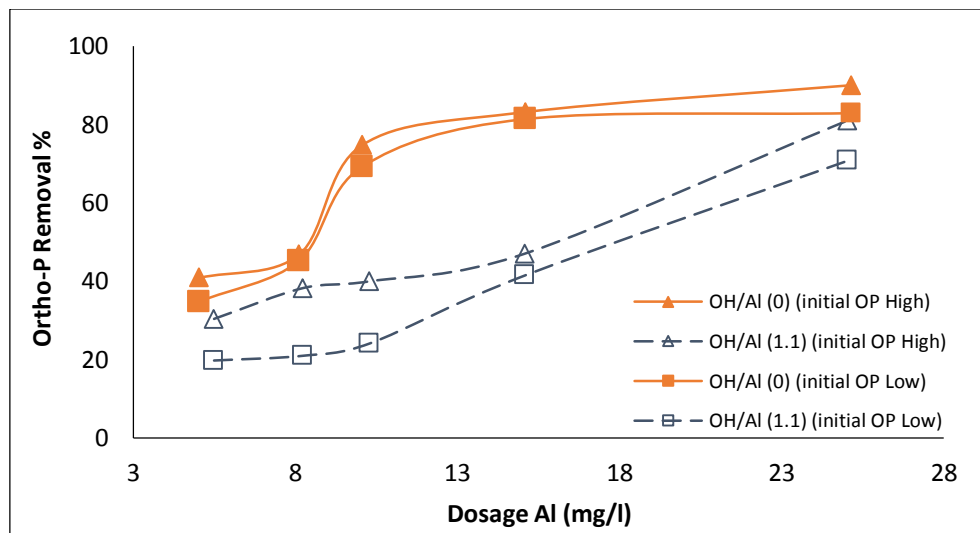
Figure 5 illustrates the difference in dosage estimates using the existing ADCS calibrated for 94% Total-P removal and maximum flow of 700 L/s (blue line) and ADCS model calibrated for 96% Total-P removal and 1300 L/s (orange line). The grey line refers to the outlet turbidity with the existing ADCS model. The figure shows that in two occasions within one month, the outlet turbidity was much higher. The modified and recalibrated ADCS model shows a better response, which is capable of reducing the outlet turbidity.

Similarly to the above observations, data presented in the Paper I confirms the ability of an ADCS to produce acceptable results at higher flow rates. The NRA has continued to show over 30% savings in coagulants compared with the flow proportional dosing, which means ADCS is an efficient tool to keep the Al:P molar ratios at a minimum. Thus the

hypothesis on the capacity of ADCS provide a flexible and efficient treatment with optimal dosages cannot be disprove.

#### 4.2 Influence of OH/Al ratio of coagulants on PAP levels in sludge

Results presented in this section related to the **Objective 2**. The aim of this section is to evaluate influence of the OH/Al ratio of coagulants on the PAP of in coagulated sludge. Ratnaweera (1992) reported the influence of OH/Al on particle and phosphate removals, where increasing OH/Al in coagulants led to comparatively less phosphate removals. It is therefore interesting to see if there is any positive or negative impact of OH/Al on PAP which can be utilized by WWTPs.



**Figure 6.** Relationship between Ortho-P removal and coagulant dosage with coagulants for high and low OH/Al in synthetic waters with high and low phosphate concentrations.

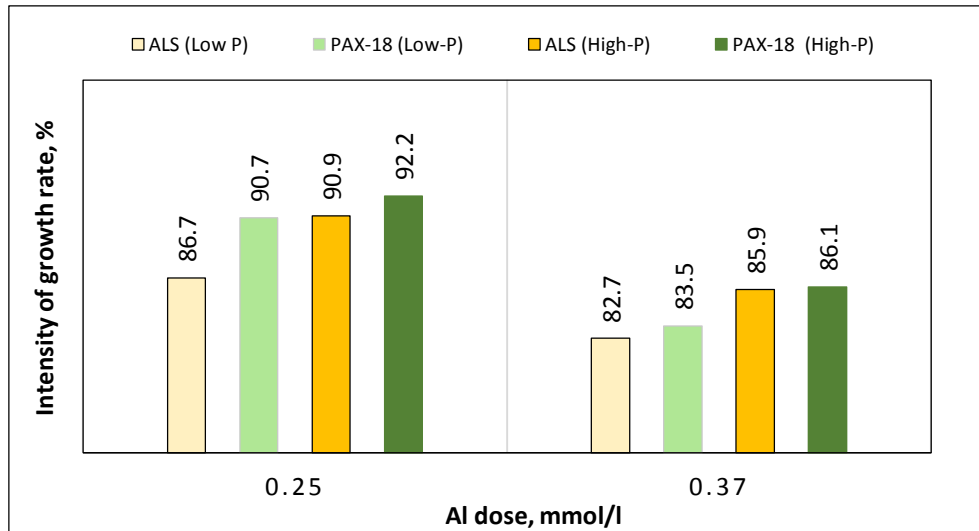
Figure 6 presents a comparison of two coagulants with different OH/Al ratios and the relationship between the dosage and Ortho-P removal. In general, higher the OH/Al ratio, the higher the dose required to achieve a comparable Ortho-P removal. This is in agreement with the observation of Ratnaweera (1992). Referring to Øgaard (2013), the coagulants with higher OH/Al shall then result in poorer PAP values, as they lead to give away more aluminium in sludge.

It also shows that the higher the phosphates in water, lower the removal rates for Ortho-P. Thus higher the amount of aluminium required to achieve comparable removal



efficiencies, at comparable content of particulate matter. This can be explained by the competitiveness and simultaneousness of the two reactions of hydrolysis and phosphate precipitation: more phosphates favour higher portions of coagulants for P-precipitation.

The difference between the treatment efficiencies with different OH/Al ratios are more visible at middle dosages, while remaining less pronounced in lower and higher dosages. This phenomenon was observed in several other experiments carried out during this study. These observations may give an insight to the coagulation mechanisms. Assuming that adsorption-charge neutralization (ACN) and the Sweep Flocculation (SWF) are the dominating coagulation mechanisms here, it is reasonable to conclude that ACN is dominant at lower dosages. At these dosages, the portion of available aluminium for P-precipitation will be less with high OH/Al coagulants, due to the completion from hydrolysis. When the dosages- as well as removal rates – are increased the SWF mechanism is increasingly dominating. This is especially evident at the highest dosages in Fig 6, where the Ortho-P removal rates approach each other in comparison to the middle area. The higher removals of Ortho-P in the middle area by low OH/Al coagulants indicate that a higher portion of Al is available for P-Precipitation in this range. While the SWF mechanism takes over when the dosage increases, the removal rates of Ortho-P continues to rise due to the overall increase in dosage. However, it seems the coagulants with high OH/Al changes dominance from ACN to SWF with increasing dosages and probably approach comparable levels of SWF preference with low OH/Al coagulants at higher dosages. Since the amount of total aluminium used was constant, it is assumed that the aluminium species (and their chemical bindings) found in the two types of sludge are significantly different. This may lead to a difference in PAP, despite similar contents of aluminium in the sludge.



**Figure 7.** Plant growth as a function of coagulant's OH/Al ratio, dosage and raw water phosphate concentration.

Figure 7 presents the growth results with two types of coagulants- with low and high OH/Al values and at low and high dosages. The general trend of decreasing PAP with increasing Al dosage is evident from the figure and in agreement with the observations of Øgaard (2013). The biomass allocation results also show a similar trend.

The results in figure 7 also indicates that higher the OH/Al, the higher the PAP. This is a trend opposite to what was noted in the discussion of the results in figure 6. This contradiction can be explained by the difference in the plant uptake of phosphates depending on the species and their chemical bonding. One explanation could be that with low OH/Al coagulants, phosphates create strong chemical bonds between Al and PO<sub>4</sub> ions, while with higher OH/Al- where the monomeric and polymeric hydrolysis species are dominated- the binding between them are less chemically strong, thus better PAP.

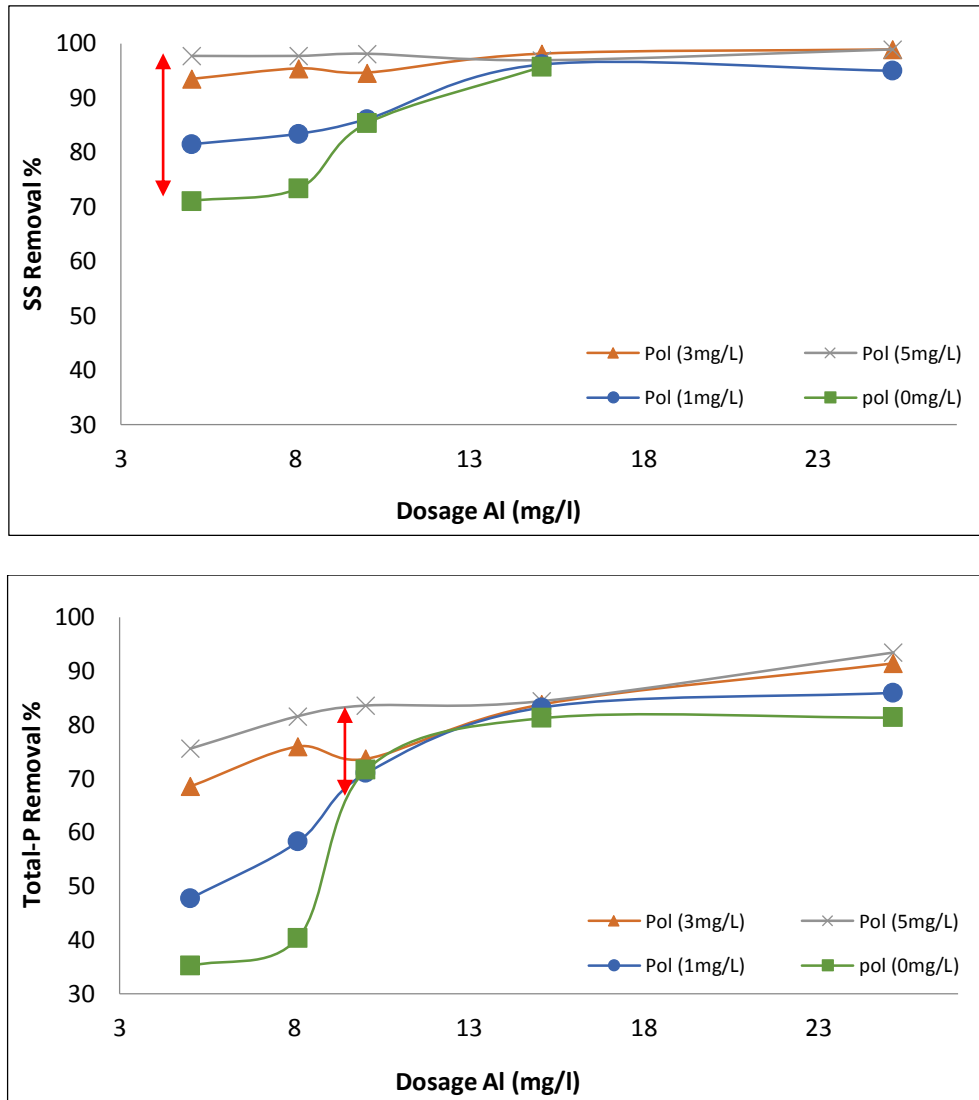
This observation also challenges the universal validity of the Øgaard's (2013) observations that PAP is inversely proportional to the aluminium or iron content in the sludge. While it seems the trend is agreeable, it seems the form which phosphates are found in the sludge, i.e. the chemical binding between the phosphate atom and aluminium atoms or species may result in different PAP values.

### 4.3 Impact of substitution of inorganic coagulants with cationic polymers in PAP levels in sludge (Paper III)

This section presents and discusses the results related to the combined coagulation of inorganic coagulants and cationic polymers presented in Paper III, and relates to the **Objective 3**. Some observations in Paper II are also included as supporting information here. The challenge with sludge from the coagulation process is that almost all aluminium and iron added during the coagulation process transfer to the sludge, while the PAP is reported to be inversely proportional to the content of these two elements.

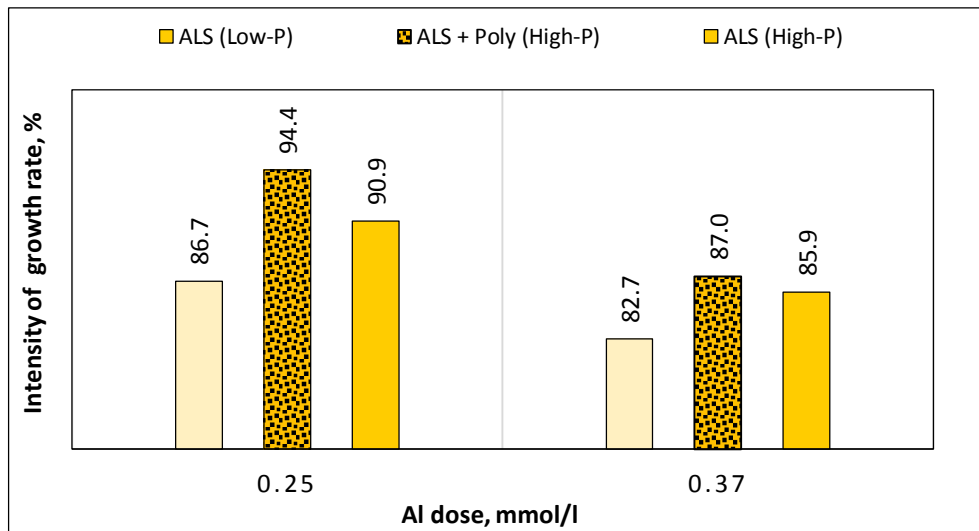
When inorganic coagulants are added to wastewater the coagulant participates in split areas; in hydrolysis to remove particles, and also in phosphate precipitation. For this reason, the molar ratios used in practice are much higher than Al:P 1:1, and often reach 3:1 and beyond (Ratnaweera 2013). If the portion of inorganic coagulants participating in particle removal can be reduced or eliminated, it is possible to reach molar ratios of Al:P closer to 1:1, thereby significantly increasing the PAP. Since the cationic polymers can efficiently remove particles, one should expect to achieve the substitution of inorganic coagulants consumed for particle removal by cationic polymers. The discussion of this section is based on the results of the jar tests with wastewater representing low-medium-high concentrations of particles and phosphates.

A series of jar tests were carried out on wastewater collected from three WWTPs in southern Norway and presented in Paper III. The results indicated at lower treatment efficiencies (around 80%) that a substitution upto 44% was possible, while it reduced to 20-25% at higher treatment efficiencies (over 90%) that also represent higher dosages of aluminium. To verify this phenomenon under more controlled conditions, a series of jar-tests were carried out with synthetic wastewater. Figure 8 shows the impact of cationic polymers on removal efficiencies of SS and Total-P. At lower aluminium dosages, the impact of cationic polymers are quite significant. The influence of cationic polymers declines with the increase of aluminium dosage. For example, at 5 mg-Al/l and 9 mg-Al/l combined with 1 mg/l of cationic polymers, the impact resulted in 80-85% removal of SS and 47-58% removal of Total-P, respectively. At higher dosages of inorganic coagulants, i.e. at 13-15 mg-Al/l, it was possible to achieve 90% removal of SS or phosphates. However, the influence of cationic polymers was drastically reduced with the increased dosage of inorganic coagulant.



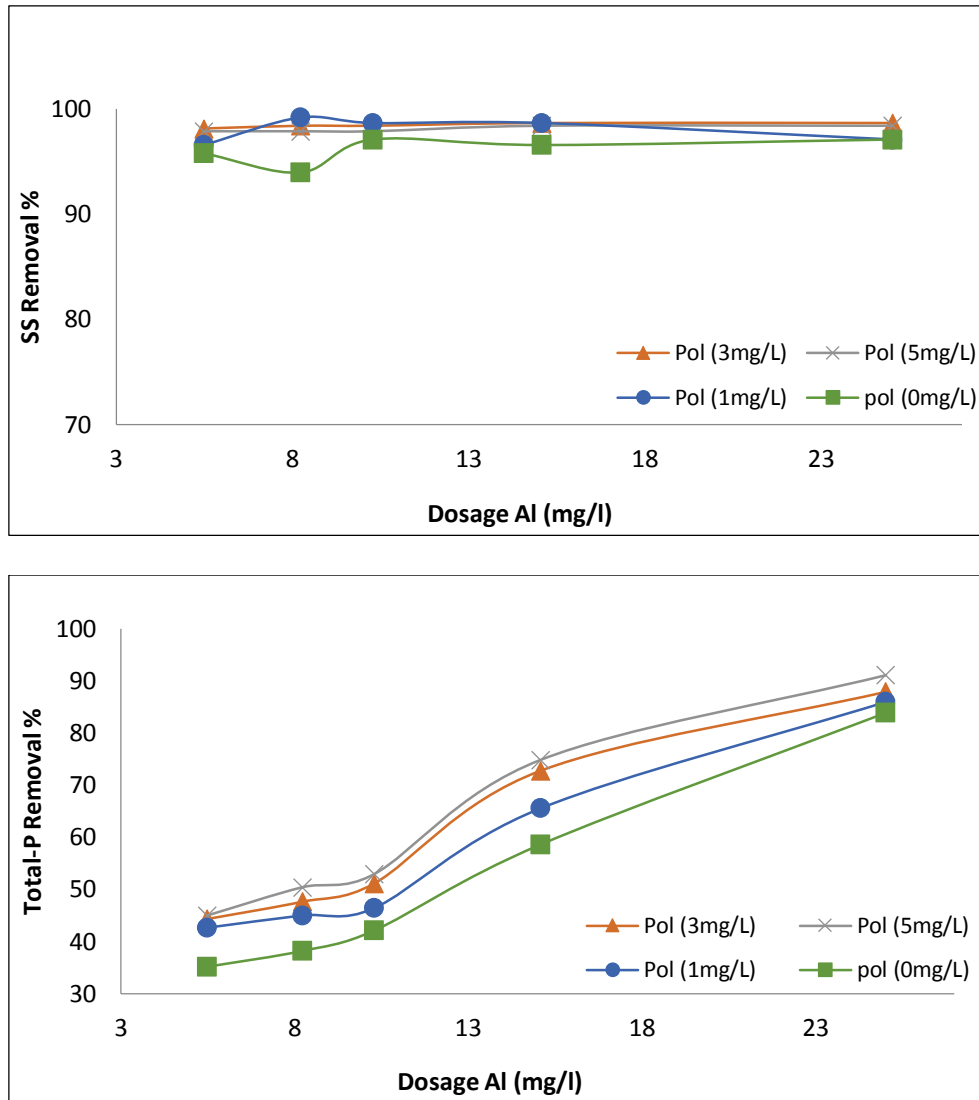
**Figure 8.** Influence of cationic polymers on SS (above) and phosphates (below) removal with low OH/Al ratio coagulant, in wastewater with high SS and high phosphates.

Figure 8 indicates the impact of cationic polymer on particle and P removal with low OH/Al ratio coagulant (OH/Al =0). It illustrates that a 75% removal of Total-P can be achieved, either with 12 mg-Al/l of an inorganic coagulant or in combination of 5 mg-Al/coagulant and 5 mg/l cationic polymer. This is almost a 60% reduction of inorganic coagulant, substituted by a cationic polymer. In several to most situations in practice it is necessary to have Total-P removals of over 90%, but then the substitution effect is almost non-existent.



**Figure 9.** Impact on growth rate intensity (an indicator for PAP), with and without cationic polymers.

Figure 9 shows the impact of cationic polymer on plant growth rate with low OH/Al ratio coagulant (ALS). A 5-8% improvement of PAP when the inorganic coagulant is combined with cationic polymer (Paper II). The improvement of PAP is higher at lower coagulant dosages, which is an agreement with the observations in figure 7.



**Figure 10.** Influence of cationic polymer and high OH/Al ratio coagulant on SS (above) and Total-P (below) removal in synthetic wastewater with medium SS and medium Total-P.

Figure 10 shows the impact of cationic polymers and coagulants with high OH/Al ratio (OH/Al=1.8). It is evident that the influence of cationic polymers was about 10% during the whole range of coagulant dosages. At the highest dosages, the difference in treatment efficiencies was not more than 5 – 7%, and the increasing polymer dosages did not improve the removal efficiencies significantly.

**Table 2.** *The dependence of SS and Total-P removal efficiencies on the cationic polymers.*

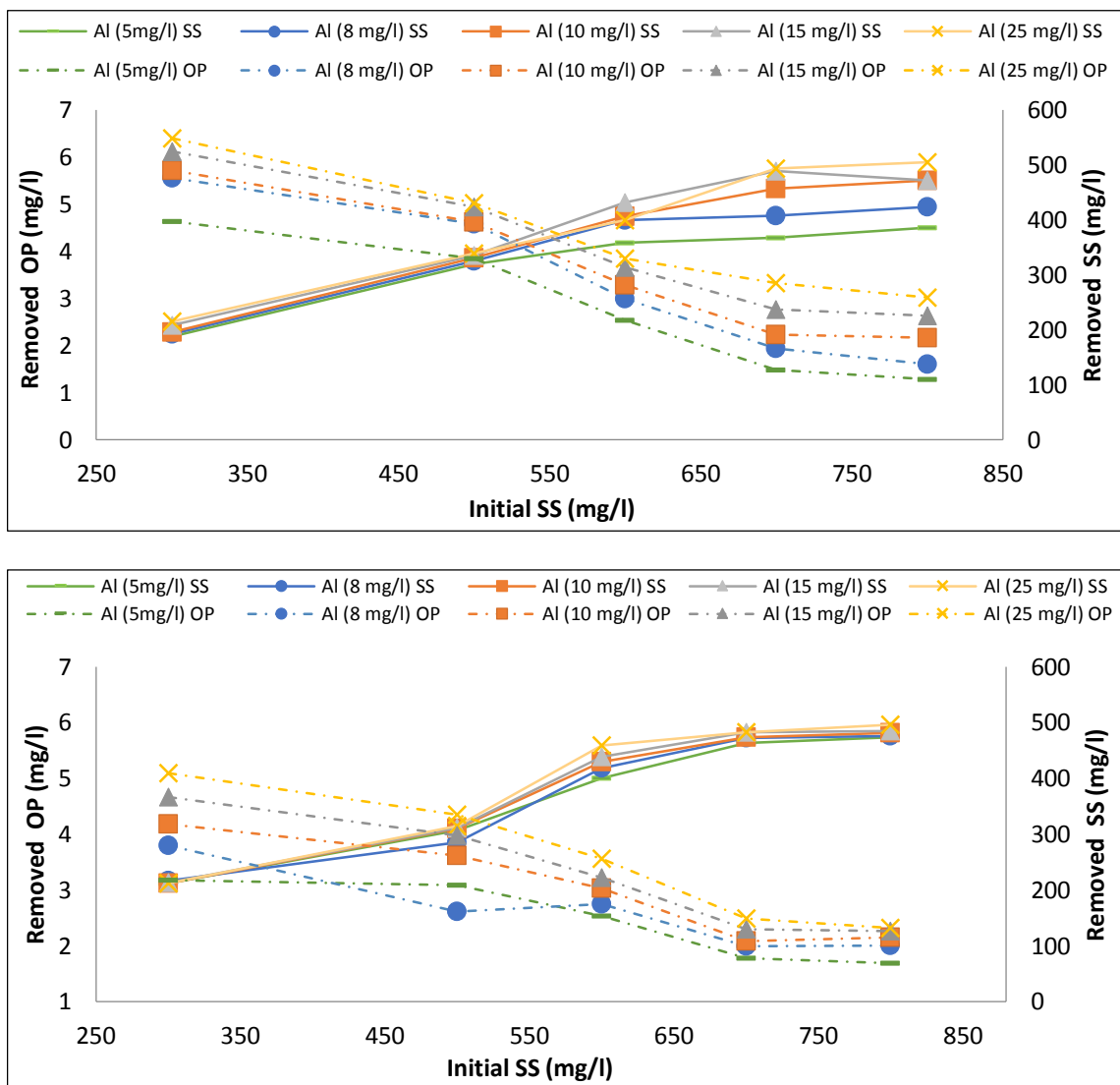
Raw water		Difference in SS removal efficiency		Difference in Total-P removal efficiencies			
Particle content	Phosphate content	with 5 mg-Al/l	with 10 mg-Al/l	with 5 mg-Al/l		with 10 mg-Al/l	
				difference	Al:P molar ratio	difference	Al:P molar ratio
L	L	4.5%	7.0%	12.0%	1.1	9.5%	2.1
M	L	7.5%	3.0%	5.0%	1.1	3.5%	2.1
M	M	5.0%	6.0%	6.5%	0.8	8.0%	1.5
H	L	32.5%	9.0%	44.0%	1.1	17.5%	2.1
H	M	25.0%	8.0%	40.0%	0.8	11.0%	1.5
H	H	25.0%	11.0%	40.0%	0.6	10.0%	1.2

Table 2 represents the summary of cationic polymer impact on removal rates at 5 and 10 mg-Al/l dosages. The molar ratio Al:P for the two dosages for six water types are given as reference data. The percentage values are represented through the average of two cationic polymer types. Waters with high particle and P contents had a significant influence (shaded values) on cationic polymers at lower treatment levels. The reduction of particles, phosphates or increase of aluminium dosages (high coagulant-to-particle ratio) caused considerable reduction of the differences.

Results, presented in Table 2, prove that higher concentrations of particles and phosphates as well as lower removal efficiencies lead to the highest level of cationic polymers impact on substitution. In the case of higher ratio of particles and/or phosphates to aluminium the dominance of ACN mechanism compared with SWF mechanisms can be expected. Lower removal rates along with lower amount of available Al-species are anticipated to cause the same conditions and results. Under the ACN mechanism it is clear that positively charged species from hydrolysis and cationic polymers have better opportunities to compete with each other in the case of “similar” conditions; hence, a higher substitution of inorganic coagulants by cationic polymers is expected. Similarly, when Al-species highly exceed the amount of particles (for i.e. water with low concentrations), the SWF mechanism is favoured and cationic polymers have less possibility to compete and substitute aluminium. At higher removal rates within these experiments the same results are observed and assumptions can be made, as the amount of Al-species versus particles or phosphates was much higher due to higher dosages.

#### 4.4 Understanding the factors influencing particles and phosphate removal efficiencies (Paper IV)

Results presented in this section relate to **Objective 4**. Results presented in **Paper IV** was obtained by experiments with different ratios of OH/Al in coagulant, with and without cationic polymers in wastewaters with different levels of SS and Total-P. In the model wastewater Total-P concentrations were equal to the Ortho-P concentrations, since the added phosphates were in dissolved form.



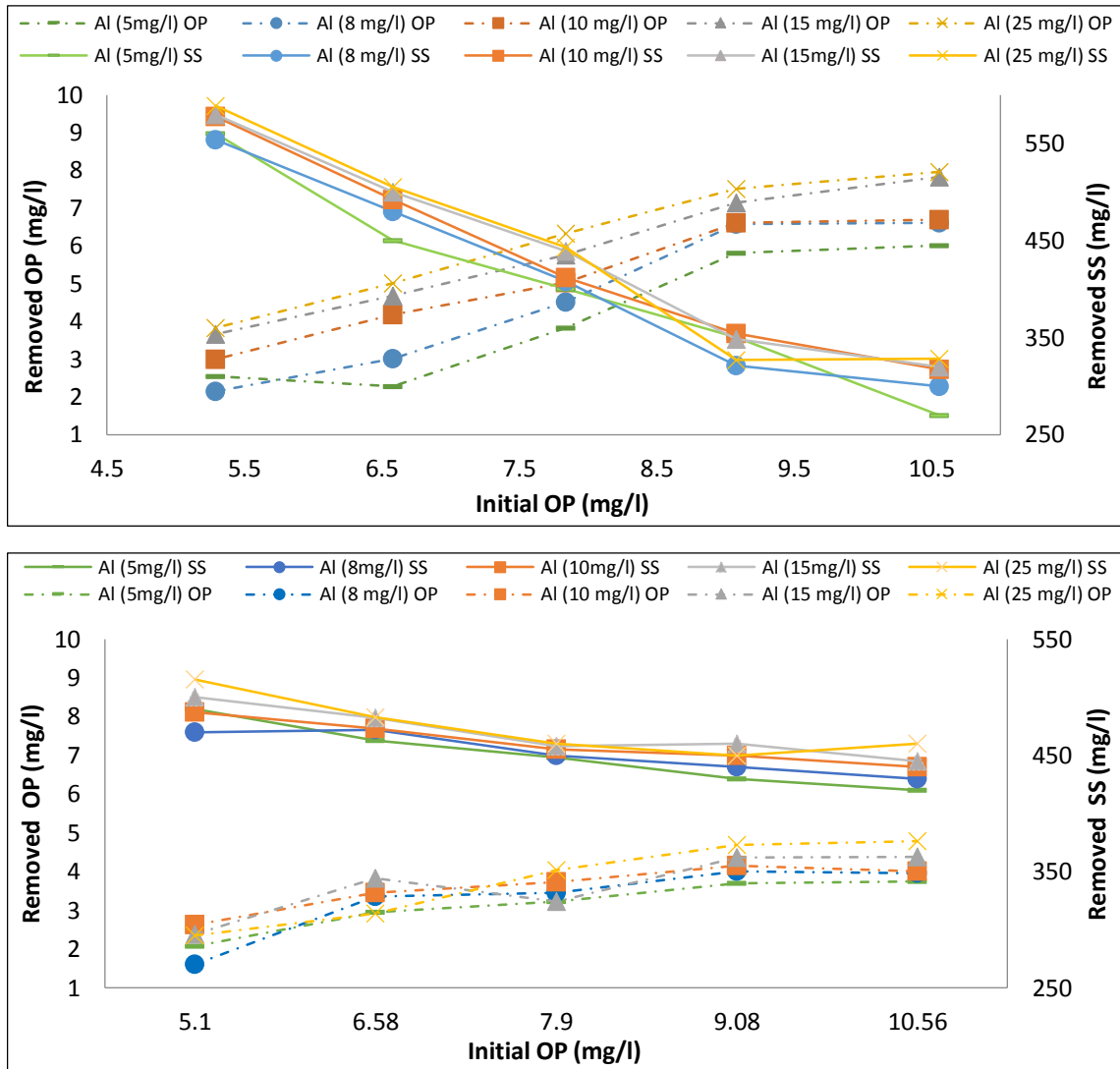
**Figure 11.** Influence of initial concentrations of SS and Al dosage on removal of SS and Ortho-P in synthetic wastewater with constant initial Ortho-P concentration at coagulation pH of 7.5 (figure above: OH/Al low coagulant and figure below: OH/Al high coagulant).



Figure 11 illustrates the relationship between initial SS concentration, coagulant dosage and OH/Al ratio for SS removal efficiencies at constant initial Ortho-P levels in model wastewater. The initial Ortho-P concentration was 10 mg P/l. Results show that the increase in initial SS concentration in raw water with constant Ortho-P level increases the SS removal efficiency, whereas Ortho-P removal efficiency decreases for both coagulants and for all the studied dosages. Thus, there are more particles compared with phosphates that compete with the P and distress the Me-P adsorption. Furthermore, SS removal at low initial SS concentration has no significant effect on OH/Al ratio, nor on the dosage of coagulant. In accordance with the schematic coagulation diagram of Stumm and O'Melia (1968), the dosage and amount of SS are in the sweep floc stage and/or near optimum coagulant dosages, which could be the reason for the described behaviour. The ACN and sweep floc mechanisms are overlapped. No re-stabilization can occur as the critical coagulant concentration could be far beyond the  $\text{Al}(\text{OH})_3$  precipitation levels.

In medium and high initial SS concentrations, the effect of coagulant dosage is significant in low OH/Al ratio coagulants, while coagulant with high OH/Al ratio has no effect at high or low initial concentrations of SS. Thus, at higher ratios of OH/Al more monomeric and polymeric hydrolysis species are present in the system. These efficiently contribute to the removal of particles by ACN.

In a WW system with lower dosages, coagulants with higher OH/Al ratios may precipitate all SS. In case of a system with extremely high concentration of SS and higher OH/Al ratio coagulant, a higher portion of coagulant may be consumed by SS removal. Furthermore, if the coagulant with low OH/Al ratio is used, the main hydrolysis product becomes  $\text{Al}(\text{OH})_3$  and the SS particles have less options for ACN than with higher OH/Al ratio coagulant at the same dosage. A portion of Al in low ratio coagulant will be used for the formation of Al-hydroxo complexes, and an additional amount of aluminium will be required for sufficient SS removal. The reason for the higher destabilization efficiency of  $\text{Me}(\text{OH})_3$  products in a coagulant with higher OH/Al ratio could be the polymeric nature and high charge character.



**Figure 12.** Impact of initial concentration of Ortho-P and Al dosage on SS and Ortho-P removal in synthetic wastewater with constant initial SS concentration at coagulation pH of 7.5 (above OH/Al low coagulant and below OH/Al high coagulant).

Figure 12 describes the relationship between initial Ortho-P concentrations of WW verses removal efficiencies of SS and Ortho-P at constant initial SS concentration of 650 mg/l. The removal efficiencies of Ortho-P increased and SS removal efficiencies decreased with the increase in the initial Ortho-P concentrations. The reactions of Al-P and Al-hydrolysis compete; when there is more SS the Al-hydrolysis is dominant, while when there is more P, then Al-P formation is dominant.

The comparison of Ortho-P removal efficiency with the OH/Al ratios of the coagulants shows that at constant initial SS concentration in the raw water the P removal efficiency change inversely proportional to OH/Al ratio of the coagulant. Thus, with high OH/Al

coagulants, the formation of Al-hydroxo-P complexes seem to be favoured, while at low OH/Al coagulants the formation of  $\text{Al}(\text{OH})_3$  and  $\text{AlPO}_4$  precipitates will be dominant. The extent of P removal with both mechanisms depends on OH/Al ratio of coagulant.

Comparing dosing methods, simultaneous dosing gives higher probability for precipitating aluminium phosphates in sludge than add-mix-separate-add-mix (sequential) dosing. This could be explained by how in sequential dosing the flocs formed in the first dosing step break during the second mixing step, thus not contribute significantly to their precipitation in the latter sedimentation stage.

A quantification of Al-P atomic bonds vs Al-OH bonds in sludge could have given further insight to the reasoning behind different impacts on PAP with different sludge. The attempts made to quantify atomic bindings with FTIR- and Scanning electron microscopy was not successful at this time due to various reasons. However, to verify some of the interesting assumptions and hypotheses raised in this thesis, it is necessary to quantify the phosphate species found in various sludge types and run growth experiments.

An ADCS using multiple water quality measurements has been developed and evaluated for a single coagulant at several full-scale water and wastewater treatment plants. Using that experience with feed-back water quality parameters and producing sludge with higher PAP is the next stage of further developing a flexible ADCS approach.

## 5 Conclusions

1. A multi-parameter based ADCS system has been in use at a wastewater treatment plant for more than 5 years; recording a reduction of 30% coagulant use and 30% sludge treatment costs. The use of the system was required to increase from 700 L/s and 94% removal of total phosphates to 1300 L/s and 96% removal of total phosphates. After modifications to the model the ADCS has confirmed its capability of achieving these targets, maintaining low Al:P ratios. Thus, the flexibility and capability of an ADCS is demonstrated as a valuable tool to retain lowest possible aluminium and iron amounts in sludge, thereby providing better PAP values. Hence, the first hypothesis, which addresses the possibility to achieve low aluminium contents, i.e. high PAP levels, with a proper dosing control system, is not rejected.

2. Sludge from raw water that contains high initial phosphates has low aluminium contents at low coagulant dosages, independently of the OH/Al ratio. Referring to the existing understanding that PAP is inversely proportional to the aluminium or iron content, this indicates higher PAP at low dosages. Coagulants with high OH/Al ratios require higher dosages of aluminium to achieve phosphate removal efficiencies comparable with coagulants of low OH/Al ratios. This suggests that coagulants with high OH/Al ratios generate sludge with low PAP. Observations were independently made on the coagulant dosage and raw water phosphate levels.

3. Plants grown with coagulated sludge from high OH/Al ratio coagulant produce higher biomass, indicating higher PAP, in comparison to sludge from lower OH/Al ratio coagulants. This is contradictory to the observations made with jar tests (conclusion No. 2) that refer to the general understanding of the inverse proportionality between PAP and aluminium content.

4. Conclusions of low PAP with high aluminium content and vice versa cannot explain the observations made in growth tests using coagulants with high OH/Al ratios, giving high growth. The possibility of generating aluminium species with variable impact on PAP could explain the apparent contradictions between conclusions No. 2 and No. 3. It is justified to believe that with high OH/Al ratio coagulants, more phosphates are found as aluminium hydroxophosphate complexes or phosphate ions adsorb on to hydrolyses species rather than

as aluminium phosphates with Al-P bonds. Hence, the current understanding of the universally inverse relation between aluminium content in the sludge and PAP is challenged. It is suggested that while it could be true for species with Al-P bonds, the relation will be different for the many other forms of aluminium found in coagulated sludge.

5. Cationic polymers can positively contribute to the substitution of inorganic coagulants by efficiently removing particles. The substitutional effect is prominent (40-60%) at treatment efficiencies up to 80% removal of phosphates on coagulants with low OH/Al ratio. The substitution impact on coagulants of high OH/Al ratios is around 10%. The impacts are negligible at higher treatment efficiencies, referring to higher dosages. Thus, the second hypothesis, which formed a platform research idea for this thesis, that the use of cationic polymers to remove particles while only using metal coagulants for the phosphates could drastically reduce metal salts consumption, is partially rejected. It may happen, but not always or with all types of coagulants or at all dosages

6. It is assumed that cationic polymers and positively charged inorganic species (Metal hydrolysis species) compete with each other in destabilization of colloidal systems. It is suggested that cationic polymers may compete successfully at low dosages per particle where the adsorption-charge neutralization mechanism is predominant. However, at higher specific dosages the ratio of aluminium to particles or phosphate is so high that the Sweep-floc mechanism seems to be preferred. During the Sweep-floc mechanism, cationic polymers have insignificant possibilities to compete with inorganic hydrolysis species.

7. Particle and phosphate removal are competitive reactions. When there are more particles (SS) the formation of  $\text{Al}(\text{OH})_3$  increases and SS removal efficiency increases. Similarly, when there is too much phosphate compared to the amount of particles the aluminium phosphate formation is favoured over the formation of hydrolysis species.

8. In practice, it is suggested that the ADCS systems and coagulants with high OH/Al ratios are used as a preferred method to obtain sludge with high PAP. The cationic polymers may contribute to reduction in the use of inorganic coagulants and thereby increase PAP. However, concepts to further improve the substitutability must be studied.

## 6 Recommendations for further studies

- This thesis research shows that increased OH/Al ratio in sludge leads to high aluminium contents in the sludge, while growth tests indicate PAP proportionally increase. The previous perceptions that generalized the inverted proportionality between total aluminium content and PAP is thereby challenged. Thus, it is necessary to establish relationships between various aluminium species in sludge and PAP.
- There is almost no understanding of the aluminium species generated during coagulation beside a general quantities relationship, often referring to molar ratios of Al:P. The speciation of species play a vital role in understanding the PAP dynamics, and therefore also the key to establishing operational strategies to produce sludge with high PAP. Quantification of Al-P and Al-OH bonds in various sludge components will provide good insight to this issue.
- Although it is confirmed that the amount of inorganic coagulants engaged either in hydrolysis or phosphate precipitation depends on the particle or phosphate content in the influent, it is not understood why cationic polymers can fully substitute the portion of aluminium coagulants engaging in particle removal. Further studies under controlled and different conditions must be carried out.
- Controlling the quality of sludge produced to secure high PAP is a significantly more logical and economically feasible solution than post treatment of sludge to increase PAP. Better understanding of the chemistry of coagulation mechanisms that depend on OH/Al ratios and particle and phosphate contents is critically important to achieving this target.

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## 8 Appendix- Publications

Paper 1:

- 8.1 Retrofitting coagulant dosing control using real-time water quality measurements to reduce coagulant consumption.

Lelum Manamperuma, Harsha Ratnaweera and Subhash Rathnaweera

Paper presented and published in conference procedures at Instrumentation, Control and Automation Conference (ICA) 2013, Narbonne, France, 18-20 September 2013.

Paper 2:

- 8.2 Effect of degree of prepolymerization of coagulant and ratio of phosphate-inorganic metal on coagulated sludge.

Lelum Manamperuma, Harsha Ratnaweera, Arve Heistad and Liubov Vasenko

Paper submitted to the International Journal of Environmental Technology and Management (IJETM).

Paper 3:

- 8.3 Coagulation mechanisms during the substitution of inorganic salts with cationic polymers to increase the sludge value.

Manamperuma, L. and Ratnaweera, H. (2015) Coagulation Mechanisms during the Substitution of Inorganic Salts with Cationic Polymers to Increase the Sludge Value. *Journal of Water Resource and Protection*, 7, 1495-1501. doi: [10.4236/jwarp.2015.717123](https://doi.org/10.4236/jwarp.2015.717123).

Paper 4:

- 8.4 Mechanisms during suspended solids and phosphate concentration variations in wastewater coagulation process.

Manamperuma, L. D., Ratnaweera, H. C., & Martsul, A. (2016). Mechanisms during suspended solids and phosphate concentration variations in wastewater coagulation process. *Environmental technology*, 1-17. doi: [10.1080/09593330.2016.1150354](https://doi.org/10.1080/09593330.2016.1150354)

## PAPER 1

Retrofitting coagulant dosing control using real-time water quality measurements to reduce coagulant consumption.

Lelum Manamperuma, Harsha Ratnaweera and Subhash Rathnaweera

Paper presented and in conference publishing procedures at Instrumentation, Control and Automation Conference (ICA) 2013, Narbonne, France, 18-20 September 2013.





# Retrofitting coagulant dosing control using real-time water quality measurements to reduce coagulant consumption

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## Abstract:

Defining the optimal coagulant dosages to suit rapidly changing influent quality is vital in reducing coagulant consumption and subsequently also to reduce sludge production. The optimal dosage depends not only on flow but also on pH, particles, phosphates and other water quality parameters. Thus, it is necessary to include as many of these critical parameters as possible in the algorithms defining the dosage in wastewater treatment plants. A multi-parameter based coagulant dosing system is described and long term operational results on full scale plants provided, showing over 30% of saving of coagulants and sludge volumes. Treatment plants with bypass lines are required to include the discharge loads of those flows in to the discharge permits of the treatment plants. Thus, the plants are evaluating if the treatment efficiencies can be increased to even higher levels during normal operational times to maintain the annual averages at required levels. The dosing control system is designed to evaluate against this. The system is then calibrated to increase the treatment efficiencies while also rapidly increasing the flow rates. The system proves to function well until it reaches limitations related to the capacities of the particle separation process.

**Keywords:** coagulation; dosing control; phosphate removal

## 1. INTRODUCTION

Over 70% of domestic wastewater in Norway is treated by chemical or chemical/biological methods (Berge and Mellem, 2012). Many wastewater treatment plants (WWTP) in Scandinavia uses coagulation, while more WWTPs in Europe and other countries also start to use coagulation. Most WWTPs in China now must remove phosphates to levels below 1 mg-P/l while some even below 0.5 mg-P/l. Coagulation represents a robust alternative to the biological phosphate removal, while the cost of the coagulants and the increase of sludge volumes due to metal hydroxide generated during coagulation remain as the biggest challenges related to coagulation.

The optimal coagulant dosage varies with the quality and quantity of the incoming wastewater. The flow, particles, phosphates and pH are acknowledged as the most influencing parameters on the optimal dosage for a given coagulant and a plant. These parameters vary widely during an hour or a day due anthropogenic and industrial activities, and they vary not proportional to each other. Thus dosing control based on one parameter will not give the optimal dosage, and to obtain required results, the WWTPs may have to dose more than the optimal dosages, or risk sub-standard effluent qualities.

Despite the knowledge and need for better dosing control in wastewater coagulation, systems integrated with several water quality parameters are scarce, even on the research scale. This paper presents the results of a novel approach based on real-time multi-parameter based coagulant dosing control, not only with remarkable

performance but also a possibility to tune the dosing control system to required removal efficiencies.

## 2. METHODOLOGY

A multi-parameter based real-time dosing control system developed by DOSCON was installed at the Lillestrom WWTP in Norway, serving about 110 000pe or 40 000m<sup>3</sup>/day. The DOSCON system has a unit which collects online water quality signals from the WWTP's SCADA system and an embedded PC with a set of algorithms which estimates the optimal dosage for any given time. The estimated dosage value is then sent to the WWTP's SCADA system to control the dosing pump.

For calibrating, partial least squares regression method is among the different regression methods used. Lillestrom WWTP's data of water quality and real-time dose was divided into 6 groups with similar number of data in each group. Each group of data was used to calibrate model algorithms, to estimate the optimal dosage using other water quality parameters, interaction effects and square effects. After running the calibrated algorithms with close observations for a specific duration, the data from the 1<sup>st</sup> model algorithms were used for the recalibration. The typical basic algorithm for estimate the optimal dosage is

Dose =  $f$  (water quality parameters, interactions of water quality parameters, squares of water quality parameters).

The generic algorithms need to be calibrated to each WWTP. After a special selection process of suitable datasets, they are analysed and relevant models are constructed using the chemometrics software Unscrambler®.

## 3. RESULTS

The concept has been in operation for over 3 years with excellent results. Fig. 1 presents the performance related to the Total-P with and without the multi-parameter based dosing control system.

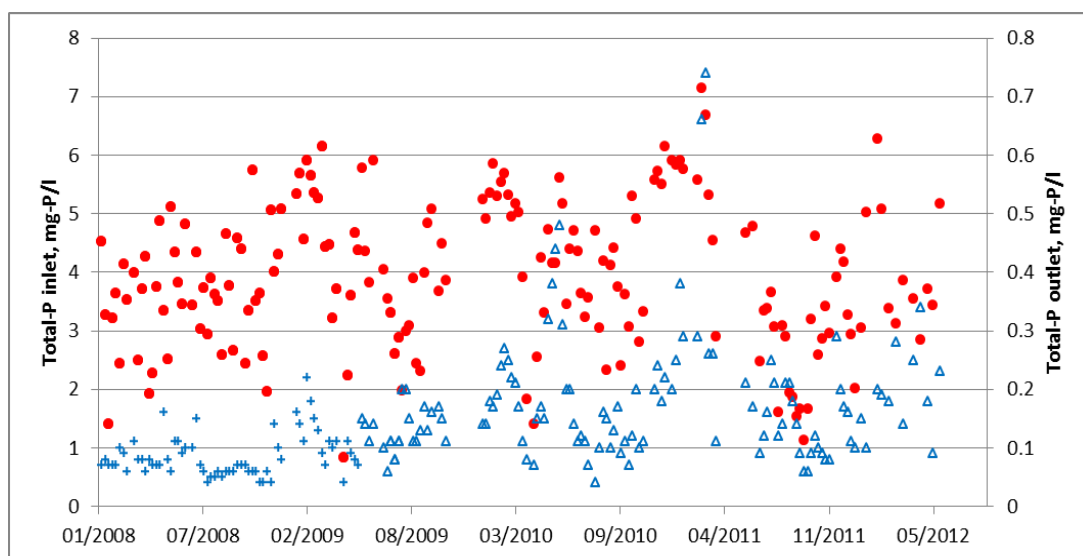


Figure 1. Total-P in the influent (•) and effluent (+) before and after (△) implementing of multi-parameter based dosing control system.

The effluent requirement for this WWTP is >94% of Total-P, thus effluent concentrations of 0.3-0.5 mg-P/l are acceptable. Due to the uncertainty of accuracy of the dosing, the WWTP was using higher dosages than required (until May 2009) resulting in effluent Total-P values between 0.05-0.3 mg-P/l. The coagulant dosing was controlled through a flow proportional system until May 2009, and a multi-parameter based dosing control system was in operation after that. Flow, Turbidity, Conductivity, pH, Temperature in the influent and Turbidity and pH in the effluent together with day and time were included in the multi-parameter based system.

The WWTP has reported over 32% savings in coagulant usage and a reduction of sludge production of over 30% were reported after 4 years of operation.

The existing discharge permit is only related to the wastewater which goes through the whole treatment process, i.e. the bypass flows during heavy rains or snow melting periods are not included. This practice will soon be changed and the WWTP anticipates not only an increased Total-P removal rates, but also these values to include also the loads of the by-pass flows. The question then was whether it is possible to calibrate the dosing control models so the required treatment efficiencies can be achieved by simply adjusting the dosage.

The WWTP at present treats only 700 l/sec, while the first task was to see if the plant could handle 1200 l/sec and maintain an average treatment efficiency of 94%. It was estimated that the algorithms has to be calibrated to remove >96% so the annual average removal will be 94%, including some bypass flows. It was necessary to recalibrate the models for the new conditions, thus the WWTP was operated with higher flow rates. The validated and selected data were used to recalibrate the model.

When the flow is as high as 1200 l/s, the Total-P concentration in the influent becomes lower, thus effluent concentrations of <0.15 mg-P/l should be anticipated to correspond to >94% removal efficiency. The WWTP does not measure the Total-P online, the turbidity was calibrated against Total-P values as shown in Fig. 2.

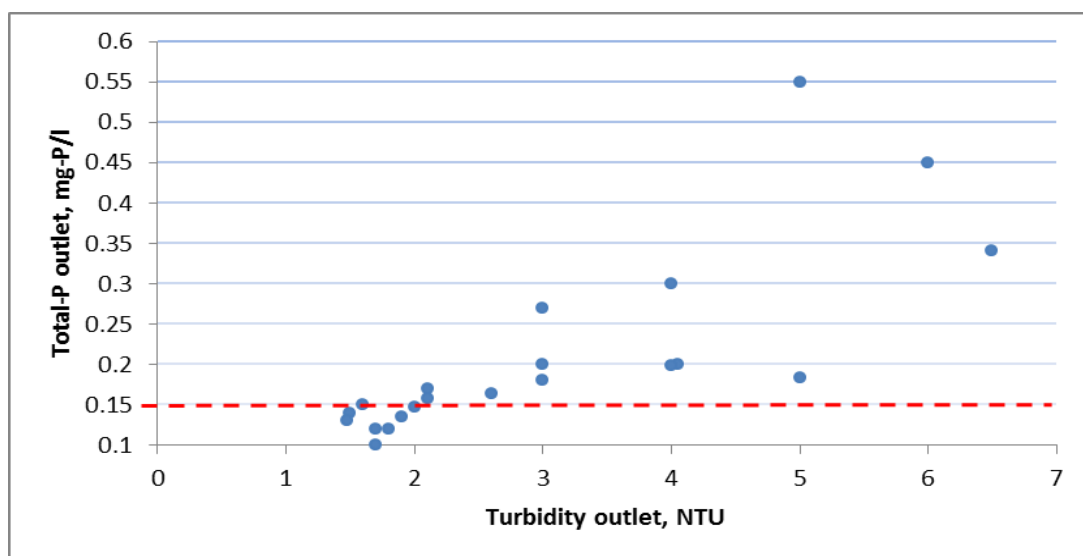


Figure 2. Total-P content in the effluent with their corresponding turbidity values.

Fig. 2 illustrates the relationship between Total-P and turbidity in the effluent for this WWTP. Thus it was concluded that it is necessary to achieve an outlet turbidity  $<2$  NTU to obtain Total-P  $<0.15$  mg-P/l. The dosage estimating algorithms were calibrated using this target parameter.

The dosing control system uses several algorithms to avoid errors caused by potential instrumental errors. The system validates the online measurements and a suitable algorithm will be used based on validated parameters (Rathnaweera, 2010). For this function, it was necessary to calibrate several algorithms.

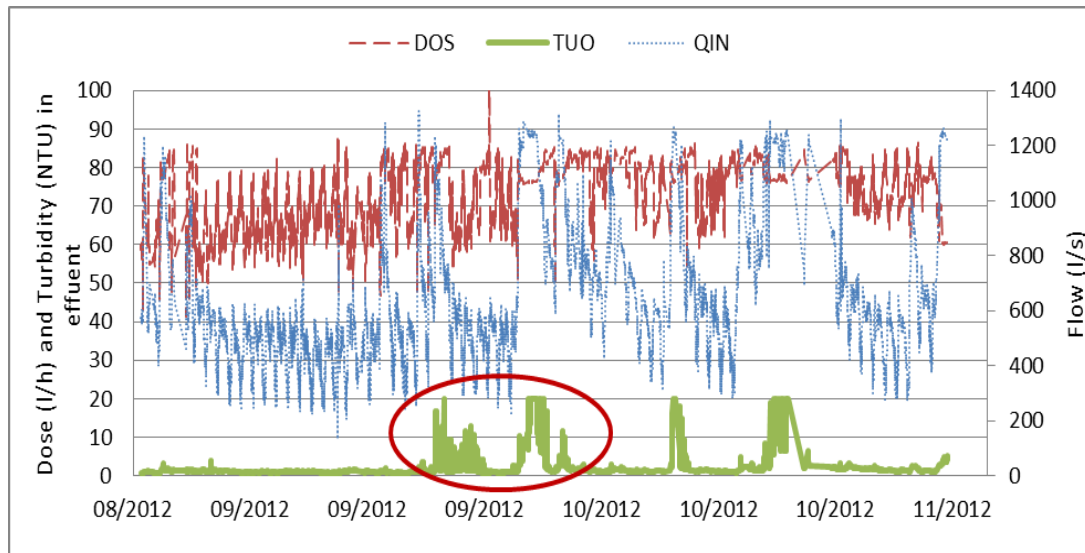


Figure 3. Operational result with recalibrated algorithms

Figure 3 shows the results with full-scale tests with recalibrated models. The dotted line in fig. 3 refers to the flow which shows that there has been several periods with flow  $>700$  l/s. The continuous line refers to the outlet turbidity, which were significantly higher during 5 occasions. The first two occasions refer to maintenance works at the plant, where one of the sedimentation tanks was out of order. This has resulted in inadequate sedimentation time. The other three situations, the flow was over 1200 l/s. The conclusion thus is that up to 1200 l/sec, it is possible to achieve necessary treatment levels just by recalibrating the algorithms.

The coagulation process it-self would be able to remove Total-P to necessary levels in influent with higher flow rates. However, it seems that the sedimentation capacity in the full scale plant becomes a limiting capacity in such situations. Further tests will be conducted to improve settleability of flocs using polymer s as flocculants.

#### 4. CONCLUSIONS

- Multi-parameter based dosing control proved to be very efficient, resulting in over 30% reduction of coagulant consumption and sludge production.
- The algorithms used in the multi-parameter based dosing control system can be calibrated to obtain necessary removal efficient with required accuracies.

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## PAPER 2

Effect of degree of prepolymerization of coagulant and ratio of phosphate-inorganic metal on coagulated sludge.

Lelum Manamperuma, Harsha Ratnaweera, Arve Heistad and Liubov Vasenko  
Paper submitted to the International Journal of Environmental Technology and Management (IJETM).





# Effect of degree of pre-polymerization of coagulant and ratio of phosphate-inorganic metal on coagulated sludge.

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## Abstract

Phosphates are becoming a limited resource as mineral Phosphorus (P) reserves are dropping down and probably will be over within next 3-5 decades. One of the solutions for this problem is to reuse the wastewater sludge as the P source in plant growth. However, the potential to increase the plant availability of phosphates (PAP) in coagulated sludge is reported to be 80-90% less than sludge from biological treatment. Effect of OH/Al ratios of coagulants and initial Ortho-phosphate (OP) levels on growth rate of plants and methods to improve PAP by different coagulants combined with cationic polymers were studied. Plant growth tests confirmed that the sludge obtained from higher OH/Al ratio coagulants have higher plant growth rates. Also combine dosing of cationic polymer with inorganic coagulants have higher biomass allocation than only with inorganic coagulants.

**Keywords** Plant availability of phosphates; Cationic polymer; Inorganic coagulants; Biomass allocation; pre-polymerization of coagulant

## Introduction

Both water and wastewater treatment consists of a sequence of complex physical and chemical processes. Coagulation is a widely used process for phosphates and particle removal in wastewater treatment. Polymeric and monomeric metal coagulants, including polyaluminium chloride (PAX) and aluminium sulphate (ALS), or polyferric sulphate (PFS) and ferric chloride ( $\text{FeCl}_3$ ) are used today in water and wastewater treatment.

In wastewater treatment, the efficient removal of phosphorus (P) is one of the main targets, as the role of P is a main factor for eutrophication of surface waters. Coagulated sludge is mainly rich in phosphates and it is no longer treated as a waste but as a resource. Potassium (K), Nitrogen (N) and P are the key elements in mineral fertilizers. P is anticipated to face a global insufficiency in the near future as the usage of P is higher than the mineral P (Cordell et al, 2009).

Number of researchers have studied the use of sludge as fertilizer. When compared with commercially available fertilizers and sludge from biological treatment, the level of plant availability of phosphorus (PAP) in coagulated sludge is disputed. Although early research (Watanabe et al., 2000; Bramryd, 2002; Gestring and Jarrell, 1982; Mengel and Kirkby, 1982; Coker and Carlton-Smith, 1986) have not found any significant difference among these sludge types, some recent research has shown that it may be as low as from 10% - 24% (Krogstad, et al 2010). Furthermore, behaviour of coagulated sludge and PAP are strongly dependent on the nature of the OH/Al ratio, phosphate concentration of wastewater, physico-chemical properties and plant species (Hylander and Simán, 2001). Continues use of aluminium/iron contaminated sludge may lead to an increase in aluminium/iron bioavailability or change in their fractionation of soil with time due to their less soluble forms initially present in sludge (McBride, 2003). Subsequently, the reduction of metal (aluminium or iron) in sludge will increase the PAP.

Hanserud in (2015) (Hanserud et al, 2015) explored the theoretical potential of wastewater sludge to supply the P fertilizer requirement of crops in Norway. It was found that if sludge to be well redistributed within Norway, the whole country could be self-sufficient in P fertilizer for all crops assessed in both in the short and the long term.

In Norway, more than 70% of wastewater is treated using coagulation as a unit process and over 85 % of wastewater sludge is used in agriculture (Berge and Mellem, 2011). The use of sludge from coagulation process as a fertilizer could be a challenge if not all phosphorous is available for plants. Thus, the farmers who are not willing to pay for sludge today, may be more reluctant to accept even free sludge if, PAP is not in the acceptable range for farming. That is why it is important to improve PAP and by this to increase value of coagulated sludge.

The aim of this study was to evaluate the PAP in coagulated sludge for plant growth. We have compared the different OH/Al ratios of inorganic coagulants and different Al-dosages to achieve similar total phosphorus (TP) removal efficiencies, partial substitution of aluminium with organic cationic polymers and discuss the influence of those factors on growth intensity of plant and biomass allocation.

## **Materials and Methods**

Experiments were carried out in the laboratory with wastewater from a small scale domestic wastewater treatment plant in Drøbak, Norway, where coagulation is used as the main treatment process and obtained sludge is delivered for agricultural purposes.

We have used two commercial coagulants from Kemira:- aluminium sulphate (ALS) and prepolymerised aluminium hydroxyl chloride (PAX-18). We have also used an organic cationic polymer from SNF Floerger FO-4350, in a working solution of 1 g/l aquatic solution. Kenwood microwave oven K23GSS11E was used for disinfection of coagulated sludge. For coagulation experiments we used Kemira Flocculator 2000 jar-test apparatus with six standard 1L beakers. The process consisted of three steps: 30 seconds of rapid mixing at 400 rpm, followed by slow mixing at 30 rpm for 10 minutes and sedimentation for 15 minutes. In combine dosing experiments, coagulant and cationic polymer were added simultaneously to the jars at the beginning of rapid mixing. The collected sludge was used for further experiments.

The initial Ortho-phosphate (OP) concentration of wastewater samples was 1.89 mg-P/l. The initial concentration of wastewater was adjusted to 3.36 (low) and 6.18 (high) mg-P/l with addition of  $\text{KH}_2\text{PO}_4$  in order to get initial TP concentrations 4 and 8 mg-P/l, respectively and used in the study.

Coagulated sludge is contaminated by almost all microorganisms found in wastewater (Tchobanoglous et al., 2003). Fungi have the strongest impact on plant growth, as under appropriate conditions some species can infect plants, others can influence the route for plant nutrient uptake. Therefore, in plant growth experiments treated sludge samples were used. For elimination of populations of plant pathogens, we microwaved sludge at 900 W heating power for 4 minutes. Our preliminary experiments showed that at 900 W 4 minutes was the minimal required time for elimination of pathogens. Additionally, content of TP and OP in all sludge samples and residual aluminium in selected sludge samples were analysed.

Analysis were carried out using Hach Lange CLK349 and Hach Lange Aluminium-Method 8012-Powder Pillows Rapid Tests by using Hach DR 3900 spectrophotometer and Hach LT 200 heating block. Randomly selected samples were analysed in several replicates to control accuracy and to reduce the analytical errors.

To compare the growth rates of plants, all the nutrients including P were provided equally in each pot. Based on total P in coagulated sludge, the amount of total P was calculated as 3 mg per pot. Parallel control pot samples were prepared with full nutrients including P, without P and without supplementary of any nutrient (which were supplied only by water).

As nutrient solution, we have chosen composition of N:P:K:Mg:Ca with ratios similar to standard commercial fertilizer content for greenhouse plant growth tests ([www.flairform.com](http://www.flairform.com)). Pre-treated wheat seeds were used for growth tests, which were disinfected with 1% chlorine water and germinated in autoclaved water for 24 hours. Bottom of each pot was covered by Watman filter paper to prevent drain off of sludge and nutrient solution. The same amount (grams) of germinated seeds and calculated amount of sludge were placed into the prepared pots. Conductivity of sludge-nutrient solution mixture in each pot was maintained between the levels of 1000 – 1100  $\mu\text{S}/\text{cm}$  by the addition of autoclaved water.

Hydroponic plant growth tests were carried out in greenhouse within 12 days and with 3 sets of replicates in each experiment including control samples. Greenhouse standard conditions were daylight from 8:00 to 22:00 at temperature 22 °C, dark period from 22:00 to 8:00 at 16 °C. Autoclaved water was used for watering during the full period of experiment and analysed parameters were the growth rate of plants and biomass allocation (BA).

The growth rate of plants was calculated by formula (1):

$$GR = H_{\text{plant}}/H_{\text{reference}} \cdot 100, \quad (1)$$

where GR - growth rate, %;

$H_{\text{plant}}$  – the height of the sample, cm;

$H_{\text{reference}}$  – the average height of the main reference plant, cm (Wood and Roper, 2000; Vasenko, 2014).

Evaluation of allocation patterns is often done for given species exposed to different environmental conditions, as it serves as an indicator of the well-being of the plant (Poorter et al., 2012). In our experiments roots-shoots ratio (biomass allocation (BA)) was determined after 12 days of growth (Poorter and Sack, 2012). Plants from the pots were harvested together with roots and separated roots and shoots carefully and then placed in a lab incubator at 110°C up to constant dry weight. Dry biomass was recorded by using an analytical balance. The mean value of biomass allocation of plants was estimated by using the formula (2):

$$R: S = m_{\text{roots}}/m_{\text{shoots}}, \quad (2)$$

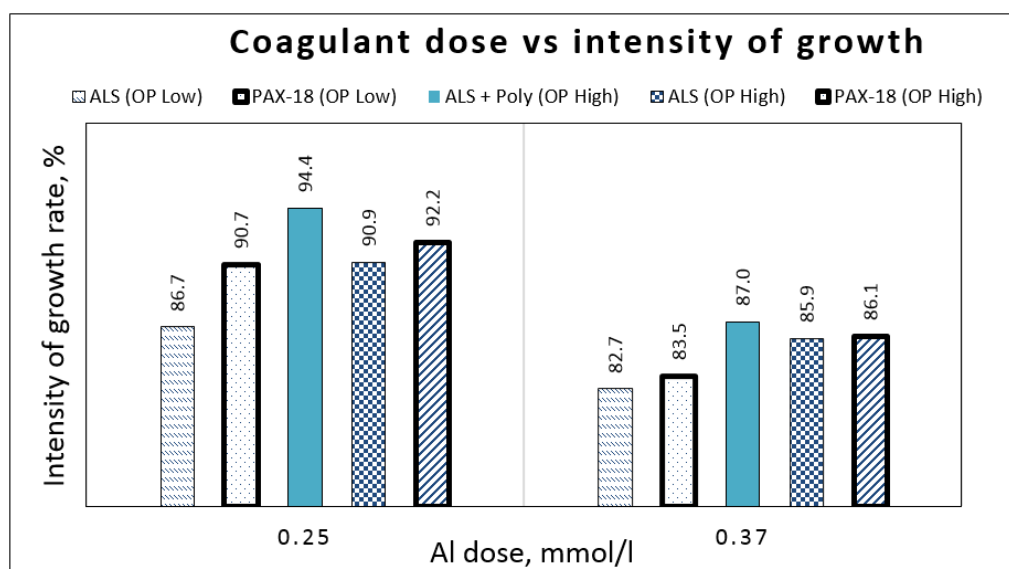
where  $R: S$  – roots/shoots ratio;

$m_{\text{roots}}$  – dry weight of roots, g;

$m_{\text{shoots}}$  – dry weight of shoots, g. (Vasenko, 2014).

## Results and discussion

Series of jar tests were carried out with 2 types of wastewater representing low and high concentrations of phosphates. The obtained sludge samples were used for hydroponic plant growth tests, carried out in climate controlled greenhouse with replicates in each experiment.



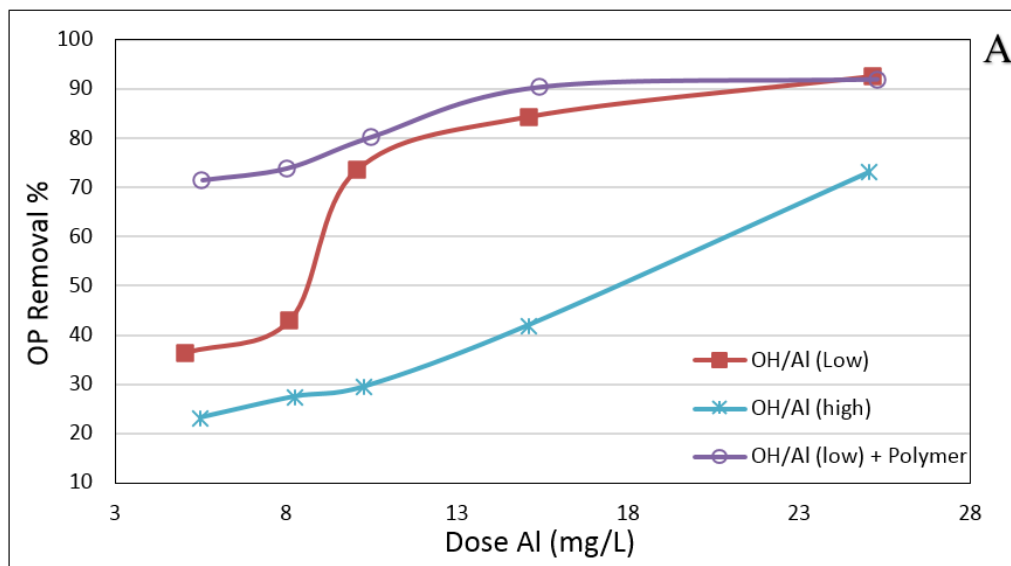
**Figure 1.** Comparison of intensity of growths on sludge obtained from wastewaters with high and low initial TP concentrations by addition of different dosages of ALS with and without polymer and PAX-18.

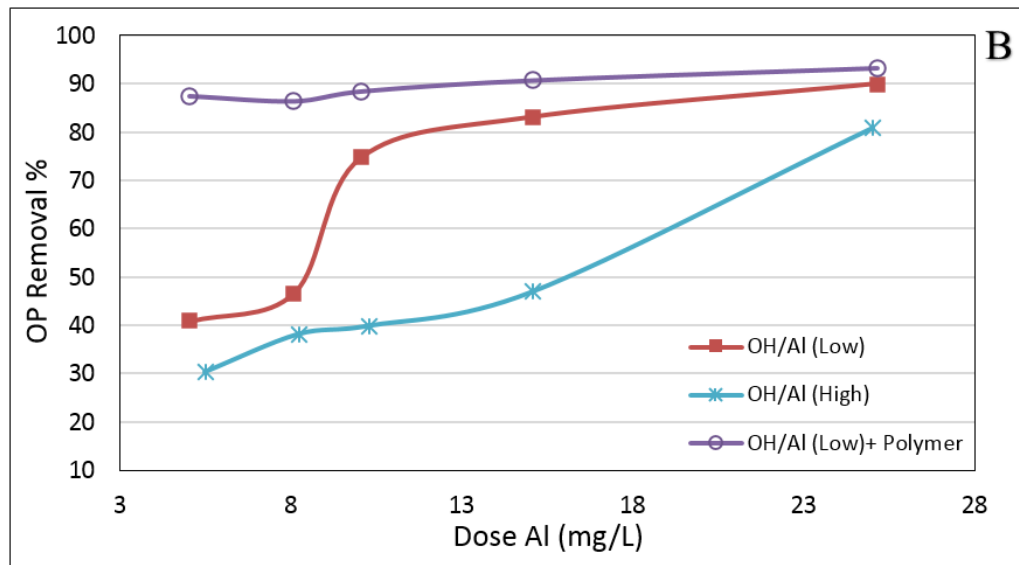
Fig. 1 shows that addition of low dosage of both coagulants to raw water with high and low TP levels resulted in higher plant growth rate than with the addition of high dosage. This could be due to intensive removal of OP due to chemical precipitation and formation of Al-phosphate complexes, which have low P release levels, under the condition of excess amount of Al and/or Al-species.

However, at the same molar Al-dosage, the sludge after coagulation with PAX-18 showed higher growth rate, compared to sludge from ALS, and consequently higher PAP level. This phenomenon can be explained by the difference in OH/Al ratio of coagulants. At low OH/Al ratio (ALS), phosphates are suggested predominantly removed by the formation of aluminium phosphates and negatively charged aluminium - hydroxo - phosphate complexes. They have strong binding between Al species and phosphate ions, which are either strongly bound with aluminium ions or entrapped in the middle of the complex and are held inside because of electrostatic attraction between negative phosphate ions and surrounding Al species. The strong electrostatic bonds made coagulated phosphates hardly available for plant uptake. Opposite to this, at higher OH/Al ratio (PAX-18), phosphates were removed mainly by adsorption of phosphate ions onto the Al-hydrolysis species. Adsorbed phosphates had weaker electrostatic interaction, thus they were assimilated by plants more easily. P uptake by plants was easier when phosphorus was adsorbed onto Al- hydrolysis products than when they were part of aluminium - hydroxo - phosphate complexes of precipitates. However, further experiments with zeta potential measurement should be made to prove the suggested hypothesis about dominant mechanisms of phosphate removal depending on OH/Al ratio of coagulant.

Fig 1 also shows that the difference of plant growth rates among the low dosages was higher than that among high dosages, which confirms that at higher dosages the impact of OH/Al ratio was weaker for both types of wastewater.

At both dosages of both coagulants with addition of polymer to high OP level, the plant growth levels were higher. The influence of cationic polymer decreased with the increase of Al- dosage. This results confirmed that combination of inorganic coagulants with cationic polymer removed more phosphates than Al alone. Phosphates removed by polymer have higher release of PAP in comparison to inorganic coagulants used alone.



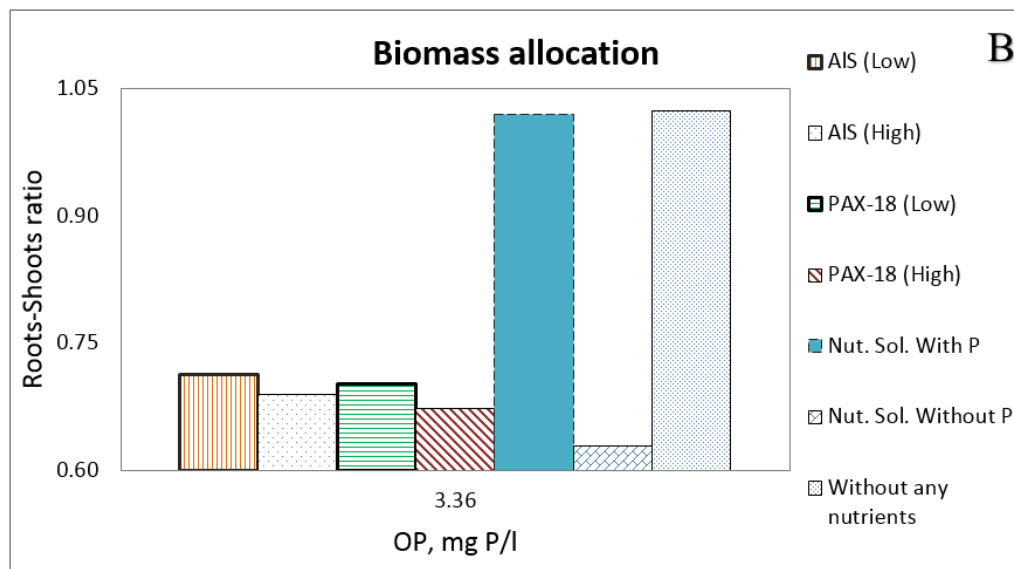
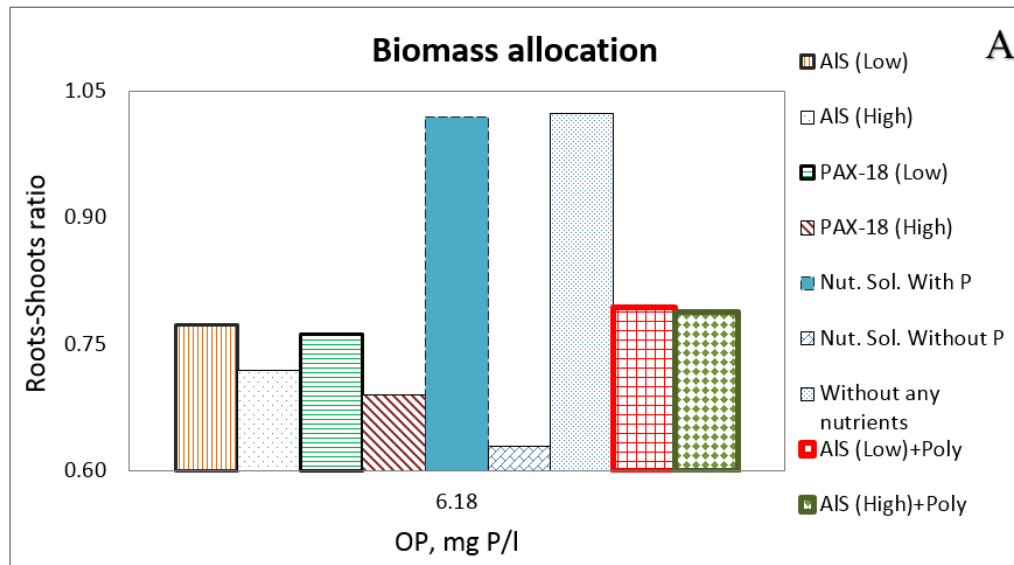


**Figure 2.** Influence of OH/Al ratio and cationic polymer on TP removal with wastewaters of high initial OP concentration (A) and low initial OP concentration (B).

Fig.2 compares the efficiencies of TP removal by coagulants with different OH/Al ratios. At lower dosages coagulant with low OH/Al ratio gave higher TP removal efficiencies than high OH/Al ratio coagulant, while the difference between efficiencies decreased with the increase of Al-dose. This means that at higher dosages the impact of OH/Al ratio was inessential for both types of wastewater. However, the highest removal efficiency was when coagulant with low OH/Al ratio was used in combination with cationic polymer.

When the coagulant dosage was low, the amount of Al- species was low then the effect of polymer was significant. It resulted in higher PAP levels of sludge coagulated by such combination, which was confirmed by high growth rates of plants.

Mechanism of organic polymer coagulants in coagulation process is yet not well documented. In this study Al/P ratio in coagulated sludge with and without polymer was 0.1367 and 0.1067 respectively. Probably, the cationic polymer trapped/bonded more Al and/or particular phosphates coagulation with simultaneous dosing and formed bigger and stronger flocs, which adsorbed particular phosphates onto the surface and sediment. Phosphates in this form had significantly higher PAP level than the Al-P bonded phosphates.



**Figure 3.** Comparison of biomass allocation of plants; nutrient solutions with and without phosphorus, dosages of coagulants with cationic polymer (A) at high OP levels and without cationic polymer (B) at low OP levels.

In this experiment all the plants were provided by all nutrients in optimal concentrations. However, each sample had phosphorous supply of different origin, thus the development of plants and roots-shoots biomass ratio were limited by the availability of phosphorous in each sample.

The results showed that roots-shoots biomass ratio (BA) in both high and low OP samples changed in the following way: control without any nutrients (water) > control with all nutrients > ALS (low) dose > sludge from PAX-18 (low) dose > sludge from ALS (high) dose > sludge from PAX-18 (high) dose > control with nutrient solution without P.

The highest BA was observed in the control samples which were grown with the addition of the nutrient solution with P and without any nutrient addition. This result can be explained by the achieving of the optimal N:P:K ratio which is necessary for plant growth. Optimal ratio was achieved due to the addition of well balanced nutrient solution in plants with addition of the nutrient solution with P. In plants without any



nutrient addition, when the plant were supplied only by water, the optimal N:P:K ratio can be explained by the internal nutrient resources of seeds. Both samples contained phosphorous in the most easily available form for the uptake, thus the BA level of 1.02 can be considered as the standard BA for that species of plant.

The second high result showed samples with sludge obtained with polymer addition. This confirms that particulate phosphates trapped/bonded by cationic polymer have higher PAP. Also samples obtained with low coagulant dosages had higher BA, including that Al:P ratio of sludge influence its PAP level. The lowest BA was in samples that were supplied by nutrient solutions without phosphorous. This can be explained by lack of P as a key element for root growth.

Furthermore, BA levels are mainly dependent on the P uptake. BA in the plants those, used the sludge of ALS coagulant was higher than the PAX-18 in high OP content waters and this effect was similar in low OP content waters. This could be due to, when OH/Al ratio was lower the phosphates removal efficiency was higher and P availability for roots was higher, so the BA levels were higher and supporting experimental evidences have been reported in the literature (Mazza et al., 2012).

Comparing the coagulated sludge by BA, the highest was when combination of polymer with both the low and the high doses of Al was used. This can be explained by the form of P release from the sludge obtained by polymer with coagulant was higher than by only with coagulant.

## **Conclusions**

The highest sludge PAP levels are achieved by the coagulants with higher OH/Al ratio and at higher dosages of coagulant the impact of OH/Al ratio is insignificant. Moreover, the sludge which was obtained from the water with high initial phosphates has higher PAP than the sludge which was obtained from the water with low initial phosphates, regardless of whether the coagulant with high or low ratio OH/Al was used.

The Comparison between PAP levels of coagulated sludge with similar TP removal efficiencies with polymer and different Al dosages showed that the effect of polymer is less significant at high Al dosages for both OH/Al ratios, as Al competes with polymer and forms strong bonded Al-P complexes. These complexes have lower PAP levels. Combined dosing formed meshi Al-polymer product which adsorbed particular P, and thus had higher PAP levels.

Controversial results were obtained in the experiments with BA measurement. Findings shows that in samples with coagulated sludge from lower OH/Al ratio coagulant the plants had higher biomass allocation than in samples with the coagulated sludge from higher OH/Al ratio coagulant. This fact confirms that the further research is needed to estimate the accurate level of PAP in sludge from coagulants with different OH/Al ratios.

## **Recommendations**

Additional experiments focused on zeta potential measurement are recommended to prove the suggested hypothesis about dominant mechanisms of phosphate removal depending on OH/Al ratio of coagulant. Preferably, these experiments to be done in wide range of dosages of coagulants with different OH/Al ratio.

In order to understand the influence of OH/Al ratio of coagulant on the PAP of coagulated sludge and to develop correlation between OH/Al, PAP and OP/Al, additional experiments are recommended with wide range OH/Al ratio and with wide range of initial OP level of water. Furthermore, different combination of different OH/Al ratios of inorganic coagulants and cationic polymers are suggested to test in order to study the influence of the various Al dosages on PAP.

Plant growth and P uptake could be highly affected by pH of sludge. Influence of coagulation pH changes with the coagulant type and dosage, so it is suggested to carryout research on wide range of dosages in different coagulants.

Growth of plants is not only limited by the PAP levels but also by the availability of the other macro and micro nutrients, residual inorganic metal concentration, and residual polymer content. Moreover, high residual metal concentration can cause a toxic effect on plants. Thus, it is recommended to analyse full range of residuals in coagulated sludge and their effect on P uptake by plants and biomass allocation. It is important to do the analysis of nutrients content in plant samples. By this, the data about the nutrients uptake will be achieved, and this will allow to analyse how the form of source of phosphorous influences its availability and parameters of plants.

Furthermore, in point of ecological view, it is recommended carry out large scale experiments to study the long term effect of coagulated sludge used on agricultural lands contaminating different inorganic metal coagulants.

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Coagulation mechanisms during the substitution of inorganic salts with cationic polymers to increase the sludge value.

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## PAPER 4

Mechanisms during suspended solids and phosphate concentration variations in wastewater coagulation process.

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# Coagulation Mechanisms during the Substitution of Inorganic Salts with Cationic Polymers to Increase the Sludge Value

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## Abstract

Phosphorus in wastewater sludge is a valuable resource although coagulated sludge reported to give only 10% of plant availability of phosphates. Since all Al and Fe added as coagulants end up in sludge, the potential to substitute them with cationic coagulants was studied. During combined coagulation, substitution possibilities up to 44% were observed with low coagulant-to-particle ratio where the adsorption-charge neutralisation (ACN) anticipated being the predominant mechanism. Comparatively high coagulant-to-particle ratio preferred Sweep-floc mechanism giving <20% substitution possibilities, though even lower values anticipated at higher phosphate removals. The cationic polymers' ability to compete with positively charged Al- and Fe-hydrolysis products was argued as the explanation for higher substitution possibilities during ACN mechanism. Substitutions can be enhanced with dual coagulation with intermediate sludge separation by avoiding competition between two coagulants.

## Keywords

Organic Polymers, Inorganic Coagulants, Plant Availability of Phosphorus, Phosphorus Removal, Coagulation Mechanisms

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## 1. Introduction

Over 70% of municipal wastewater in Norway is treated with a coagulation process [1] which annually consumes about 60,000 tons of inorganic coagulants consisting with 5% - 18% of aluminium or iron [2]. These coagulants remove phosphorus very efficiently from wastewater thus solve a serious environmental problem. Norway has invested heavily in chemical precipitation as the main wastewater treatment process to manage eu-

trophication of the lakes and rivers.

Wastewater sludge is no longer treated as a waste, but a resource. Over 70% of wastewater sludge in Norway is now used in agriculture benefiting the high content of nitrogen and phosphorus [1]. Phosphorus, which is a key element in mineral fertilizers, is anticipated to face a global deficit in the near future. The estimates show that the demand of phosphorus will exceed the supply by 2035 and the mineral phosphorous will disappear within the next 50 - 100 years [3]. The phosphorus prices has doubled since 2007, while there were periods with 800% price increase due to the scarcity in supplies [4].

However, there is a challenge with sludge from coagulation processes: Almost all aluminium and iron added during the coagulation process are transferred to the sludge. The plant availability of phosphorus (PAP) is significantly reported to be reduced in sludge from the chemical treatment plans; particularly where aluminium or iron salts is used as the precipitant. Krogstad in 2010 [5] reported that the PAP of sludge from wastewater treatment plants (WWTP) using aluminium and iron coagulants were about 10% and 24% respectively, compared to the sludge from biological treatment plants and mineral fertilizers [6].

Previous studies on PAP of coagulated sludge have reported that there is no significant difference of PAP in coagulated sludge and mineral fertilizers [7]-[11]. However, several recent studies have indicated that the higher the content of aluminium or iron in sludge, the lower the PAP [12]. Plant growth studies has documented that the content of aluminium or iron in sludge is inversely proportional to the phosphorus uptake by plants [13]. Thus, it is concluded that reduction of aluminium or iron in sludge will increase the PAP.

This paper presents results of attempts to reduce aluminium and iron content in sludge by substituting inorganic coagulants with organic coagulants, and discusses the limiting factors together with influence of coagulation mechanism.

## 2. Material and Methods

Part of the experiments was done in the laboratory with synthetic wastewaters enabling better replicability as well as the possibility for manipulating the composition of wastewater for various experimental conditions. We have chosen a synthetic wastewater composition representing common wastewater conditions and which have been successfully used in previous experiments [14]. For the current experiments wastewater with two variable phosphate contents and three particle contents were used. The properties of wastewaters are given in **Table 1**.

A part of experiments were carried out on domestic wastewater from three WWTPs in the Oslofjord area: Tønsberg WWTP, Sandefjord WWTP and Larvik WWTP. All three plants use coagulation as the main treatment process and deliver the sludge for agricultural purposes.

All used chemicals were pure chemicals from Merck and VWR Prolabo apart from humic acid, which was from Aldrich. Dry full-cream milk powder from Viking and potato starch from the Norwegian potato industries were used. Commercially available Aluminum Sulfate solution from Kemira (KEMIRA ALS) and 1 g/l solutions of commercially available polymer (FO-4240) from SNF Floerger were also used. The Kemira ALS solution is an inorganic salt ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ) with very low iron concentrated and commonly used in potable water and wastewater treatment applications and the FO-4240 is a high molecular weight and low charge density (cationicity 20% mol) organic cationic polymer. Flocculant solution was vigorously homogenised with a magnetic stirrer until the flocculant was completely dissolved. Commercially available prepolymerised aluminium coagulant (KEMIRA PAX-XL-61) aqueous solution and Ferric Chloride Sulfate (KEMIRA PIX-318) from Kemira were used as coagulants with some experiments with domestic wastewater, enabling comparison with present full scale practices at WWTPs.

**Table 1.** Typical properties of two synthetic wastewater samples.

	High phosphates	Medium phosphates	Low phosphates
Turbidity (NTU)	476	480	202
Total Phosphorus (mg/L)	9.9	7.53	199
Suspended solids (mg/L)	480	480	5.4
Ortho Phosphate (mg/L)	6.06	3.86	2.57

Analysis were carried out using Hach Lange CLK349 and CLK350 rapid tests using Hach DR 3900 spectrophotometer and Hach LT 200 dry thermostat. Turbidity was measured by Merck Turbiquant 3000 IR while SS was measured using Norwegian standard methods.

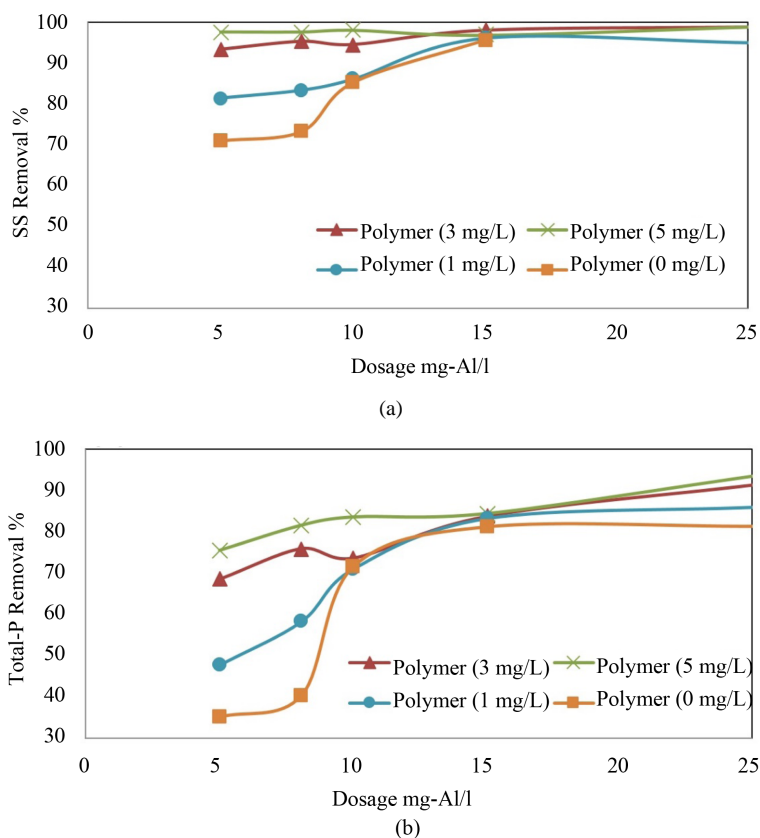
Coagulation process with inorganic salts significantly depends on the pH, which is reduced after coagulant addition due to the hydrolysis. The coagulation pH was held constant during the tests independently on the coagulant dosages by adjusting the raw water pH to result in the desired pH, which was 7.5 in this series of experiments.

The coagulation experiments were carried using a Kemira Flocculator 2000 jar-test apparatus with six standard 1 L beakers. Samples were rapidly mixed at 400 rpm for 30 seconds followed by slow mixing at 30 rpm for 10 min, and then sedimentation for 15 min. At the beginning of the rapid mixing, Al- or Fe coagulants and cationic polymer (FO-4240) were added simultaneously to the jars. After sedimentation, 180 ml of supernatant was taken as sample for further manual analysis. Inorganic coagulant dosage ranges suitable for wastewater types were varied while cationic polymer dosage range was kept constant between 0 to 7 mg/l. Turbidity, SS, pH, total phosphates (Total-P) and ortho phosphates (Ortho-P) were measured in the supernatant. Randomly selected samples were analyzed in several replicates to control accuracy and to reduce the human errors.

### 3. Results and Discussion

We have carried out series of jar tests with 6 types of wastewater representing low-medium-high concentrations of particles and phosphates. **Figure 1** shows the results for wastewater with high particle and phosphate contents.

Particle and phosphate removals in **Figure 1(a)** and **Figure 1(b)** are comparable to each other, and show that at lower aluminium dosages, the impact of cationic polymers are quite significant. The influence of cationic polymers diminishes with the increase of Al-dosage. For example, an 80% removal of SS or 50% removal of



**Figure 1.** Influence of cationic polymers on SS (a) and phosphates (b) removal with aluminium sulphate, in wastewater with high SS and high phosphates.

total-P was possible either with 9 mg-Al/l or 5 mg-Al/l combined with 1 mg/l of cationic polymers. To achieve 90% removal of SS or phosphates was possible with 13 - 15 mg-Al/l. However, the influence of cationic polymers was insignificant. We have repeated the results with two cationic polymers and the results were analogical.

**Table 2** summarises the impact of cationic polymers on removal rates at 5 and 10 mg-Al/l dosages. Molar ratio Al: P for the two dosages for six water types are also given for reference. The percentage values are given as the average of two cationic polymer types. Waters with high particle and phosphate contents had a significant influence (shaded values) by cationic polymers at lower treatment levels. With the reduction of particles, phosphates or increase of aluminium dosages (high coagulant-to-particle ratio), the differences became much less significant.

**Figure 1** and **Table 2** confirm that the impact of cationic polymers are largest when there are more particles and phosphates (low coagulant-to-particle ratio) as well as when the removal efficiencies are lower. These jar tests were done with simultaneous addition of Al coagulant and cationic polymer, thus a competition between the species of the two coagulants can be anticipated. When there are more particles and/or phosphates compared with the Aluminium, the dominance of adsorption-charge neutralisation (ACN) mechanism compared with Sweep-floc mechanisms can be anticipated. When the removal rates are lower, the amount of Al-species available is also lower thus the same conditions and results can be anticipated. When the ACN is the dominant mechanism, it is obvious that positively charged species from hydrolysis and cationic polymers have better opportunities to compete with each other under “similar” conditions; thus we can anticipate a higher substitution of inorganic coagulants by cationic polymers.

Similarly, when there is too much Al-species compared with the amount of particles (for e.g. water with low concentrations), the Sweep-floc mechanism is favoured and cationic polymers have less possibility to compete and substitute aluminium. The same situation occurs at higher removal rates under these tests, as the amount of Al-species versus particles or phosphates were much higher due to higher dosages, thus a similar situation occurs.

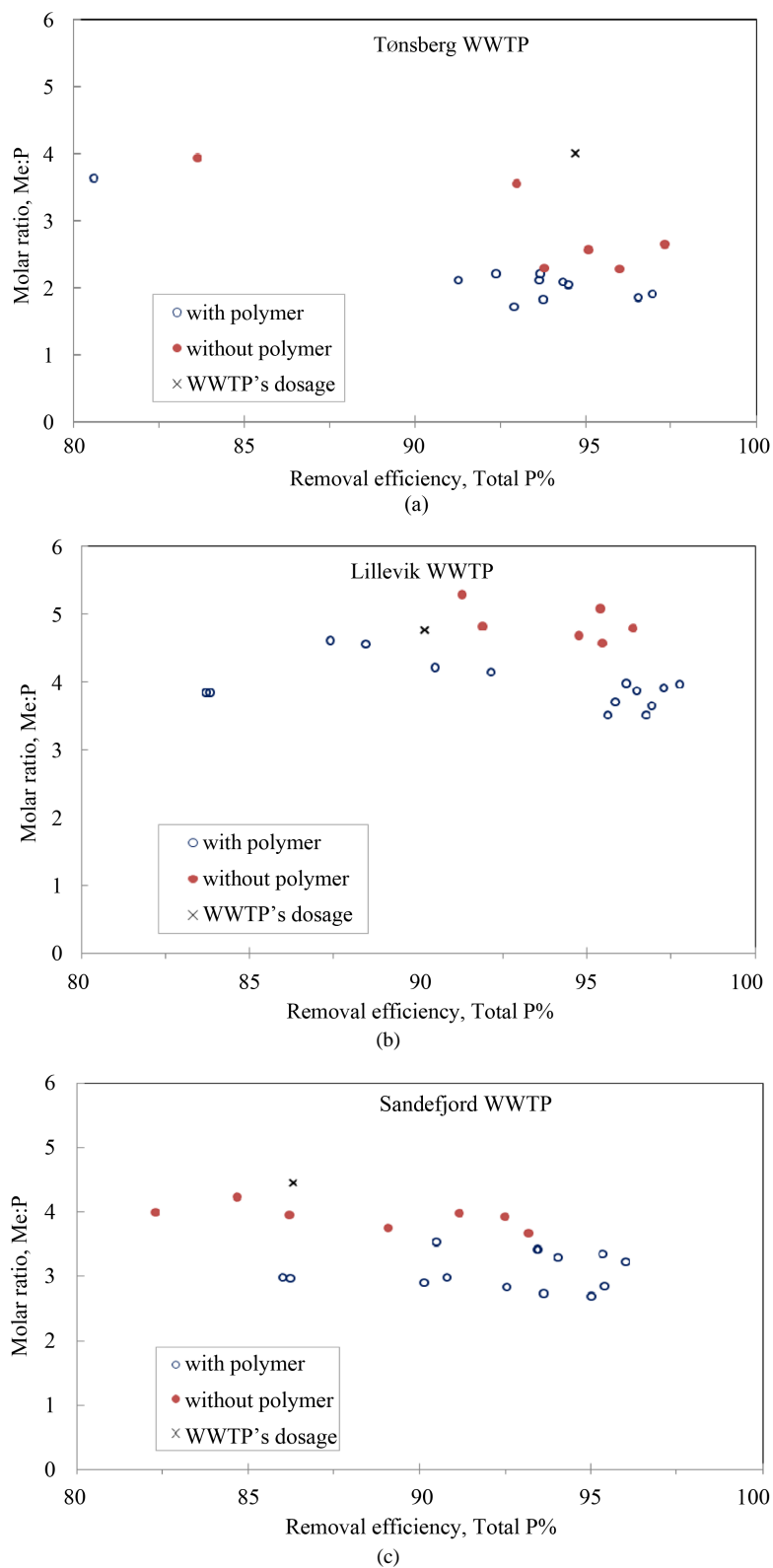
This concludes that for the extremely high SS and phosphate removal rates which are anticipated in Scandinavian WWTPs, it will be difficult to obtain significant reduction of aluminium and iron coagulants with cationic coagulants, when both coagulants are added simultaneously.

Nevertheless, if the two coagulants are added separately, it would be possible to achieve a significant substitution of aluminium with cationic polymers as there will be no competition between them. However the downside then will be the need for infrastructure and operational modifications to accommodate two coagulation stages.

Additional jar tests were carried out using domestic wastewater samples from three WWTPs, and the results are presented in **Figure 2**. The removal efficiencies of phosphates are depicted as a function of molar ratio between Al or Fe to P. In these experiments we have used both aluminium and iron coagulants interchangeably but the results are presented in a comparable manner as molar ratios.

**Table 2.** Influence of cationic polymers on SS and Total-P removal efficiencies.

Raw water		Difference in SS removal efficiency		Difference in total-P removal efficiencies			
Particle content	Phosphate content	With 5 mg-Al/l	With 10 mg-Al/l	With 5 mg-Al/l		With 10 mg-Al/l	
				Difference	Al:P molar ratio	Difference	Al:P molar ratio
L	L	4.5%	7.0%	12.0%	1.1	9.5%	2.1
M	L	7.5%	3.0%	5.0%	1.1	3.5%	2.1
M	M	5.0%	6.0%	6.5%	0.8	8.0%	1.5
H	L	32.5%	9.0%	44.0%	1.1	17.5%	2.1
H	M	25.0%	8.0%	40.0%	0.8	11.0%	1.5
H	H	25.0%	11.0%	40.0%	0.6	10.0%	1.2



**Figure 2.** Removal efficiency of total-phosphates in wastewater from three WWTPs with and without cationic polymers. Top: Tønsberg WWTP, middle: Lillevik WWTP; bottom: Sandefjord WWTP.

The filled circles in **Figure 2** present the tests without polymers and empty circles refer to tests with cationic polymers. The single cross in each figure refers to the dosage which the WWTP was using at the sampling time. In all three WWTPs this ratio was between 4 and 5, which is quite high compared with the synthetic wastewater. A survey among average molar ratios used in ten Norwegian WWTPs revealed values between 2.0 - 5.0 with exception of one WWTP [15]. Compared with the theoretical requirement of 1 mole of aluminium per 1 mole of phosphates in aluminium phosphates, these values are much higher. On the other hand, the Al: P ratio will always be higher than 1 during the efficient phosphate removal by coagulation, as a part of aluminium end up in aluminium hydroxide making it unavailable for phosphate removal [16].

The task is to reduce as much as possible aluminium or iron dosage during coagulation as they will always end up in sludge. **Figure 2** shows that 20% - 25% of aluminium or iron coagulants could be substituted if the anticipated treatment efficiencies are 85% - 90%. In most situations, the phosphorus removal requirement is well above 90%, indicating that the substitution possibility will be lower than 25%. Such a low substitution values may be not worth the trouble of having two coagulants, while dual coagulation with separate separation will give much better substituting opportunities.

Comparing the results from the synthetic wastewater, it becomes clear that better treatment efficiencies were possible with synthetic wastewater at lower coagulant dosages. This due is to considerably lower phosphate concentrations in domestic water during the specific sampling period. Considering the molar ratios and the discussion on coagulation mechanisms with synthetic wastewater, it is reasonable to assume that all tests presented in **Figure 2** were running under the Sweep-floc condition, which will also make it difficult to increase the substitution by a cationic coagulant.

#### 4. Conclusions

Studies show that the reduction of aluminium and iron in sludge will proportionally increase the plant availability of phosphorus in coagulated sludge. Since all aluminium and iron used in coagulation will go over to sludge substituting these ions with cationic polymers during coagulation would be a potential solution.

It is assumed that cationic polymers and positively charged inorganic species (Metal hydrolysis species) compete with each other in destabilisation of colloidal systems. It is anticipated that although the cationic polymers may compete successfully at low dosages per particles where adsorption-charge neutralisation mechanism is predominant. However at higher specific dosages, the ratio of aluminium to particles or phosphate is so high that the Sweep-floc mechanism will be preferred. During Sweep-floc mechanism, cationic polymers have insignificant possibilities to compete with inorganic hydrolysis species.

Very good substitution possibilities up to 44% were observed at lower treatment efficiencies or highly concentrated wastewater, where the amount of particles per unit coagulant is assumed to be low enough to make the adsorption-charge neutralisation as the predominant coagulation mechanism.

The substitution of up to 20% was possible during other situations. Since Scandinavian WWTPs require phosphate removals well above 90%, the substitution possibilities with combined coagulation assumed to be low.

Cationic polymers have documented the possibility of removing particles-thus dual coagulation with intermediate sludge separation could be an interesting operational concept where the use and treatment efficiencies with organic coagulants could be maximised thus the need for inorganic coagulants will be minimised.

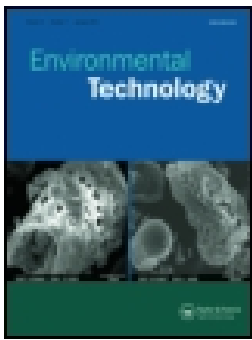
Further research to quantify the hypotheses is required and recommended.

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## Mechanisms during suspended solids and phosphate concentration variations in wastewater coagulation process

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### ABSTRACT

Coagulation–flocculation process is one of the most commonly used treatment process in water and wastewater treatment. Particles (PA) and phosphates (P) removal are the main objectives in wastewater coagulation. There is a general agreement on the dominant mechanism of PA and P removal during coagulation. While it is agreed that the PA and P removal reactions are competitive and takes place simultaneously, there is no clear understanding on the ratio of distribution of coagulants among the PA and P removal. The ratio can be significantly influenced by the content of PA and P, in addition to other water and coagulant quality factors. This paper attempts to provide a qualitative ratio of coagulant distribution based on PA:P proportion in raw water and OH:Al ratio in coagulants.

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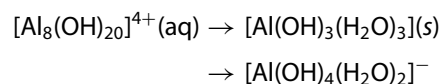
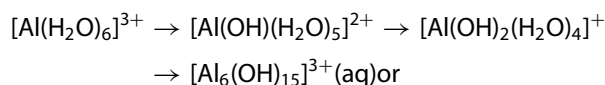
Coagulants; coagulation–flocculation; particles; phosphates; coagulation mechanisms

### Introduction

Coagulation is one of the most important process in water and wastewater treatment as it can efficiently remove suspended solids (SS) and phosphates (P) from raw water.[1–4] Coagulants are used in coagulation process. The most commonly used multivalent metal (Me) ions are calcium, aluminum and iron. There are several chemical and physical competitive reactions that occur when a Me salt is added to a colloidal system. The Me-ions are immediately surrounded by water molecules and Me-aqua complexes are rapidly formed. Then the complexes undergo a series of rapid hydrolytic reactions to form charged polymeric or oligomeric hydroxo-complexes of various structures.[5] One of the successive reactions caused by the addition of Me coagulant into a WW system are hydrolysis reactions of the Me salts. The hydrolysis products of Me salts are essential for particle destabilization which can be found in literature.[6] In the case of using conventional coagulants such as  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{FeCl}_3$ , amorphous  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$  are the predominant hydrolysis species in water treatment practice.[7]

All  $\text{Me}^+$  ions are hydrated to some extent in water. However, it has been observed that intermediate hydrolysis reactions of Al (III) are much more complex. The comprehensive chemistry for the formation of hydrolysis reactions and products is not well-understood.[8] A

number of alternative formation sequences have also been proposed by Letterman.[9]



Possible combinations of the various hydrolysis products are endless. Polynuclear hydrolysis products can be prepared in significant amounts under certain conditions. The best known of this is  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ , which can be formed by controlled neutralization of aluminum salt solutions. An important fact is that one or more hydrolysis products and/or polymers may be responsible for the observed action of Me ion. The exact chemical reaction or the nature of the hydrolysis products in wastewater particle and P removal is not clear yet. The chemical reaction of phosphorus with Me salts in a liquid environment is complex. The classic model reaction of an Me reacting with P to produce a metal-phosphate precipitant ( $\text{MePO}_4(\text{s})$ ) does not occur under the conditions in a wastewater treatment plants.[10,11]

A large number of investigations of P removal by Me salts have also been conducted by many researchers and several qualitative and quantitative models documented. [12] The main difficulty of explaining the P removal

process in wastewater treatment with Me coagulant is simultaneous particle destabilization in the colloidal system. The understanding of coagulation mechanism of P removal by using Me salts leads to the direct formation of insoluble  $\text{MePO}_4$  and Me-hydroxy-phosphate complexes [13]. When Me is salt dosed into water, a range of Me-hydrolyzed species are formed, and hence the species that can react with the  $\text{PO}_4$  ions will be a range of hydrolyzed products, including the metal-hydroxide, rather than the simple Me ions. P forms bonds with the Me-hydroxyl-complexes [14], which is the topic of this research.

A group of researchers have investigated P removal with wide range of coagulants and documented that the higher the OH/Me ratio of coagulant, the greater the amount of coagulant dose was required for P removal.[12,14–16] Another group of researchers claim that the efficiency of P removal depended on the charge density of the metal-hydrolyzed species.[17–20] In the study of Galarneau in 1997, it is concluded that removal efficiency of  $\text{PO}_4$  ions depends significantly on  $\text{Al}(\text{OH})_3$ . Galarneau explained that the adsorption mechanism involves sorption of the  $\text{PO}_4$  ion onto  $\text{Me}(\text{OH})_3$  no matter how the  $\text{Me}(\text{OH})_3$  is provided, either from direct dosing Me to the water or from Me-hydroxide precipitates.[21] The removal efficiency of  $\text{PO}_4$  ions using Me-salts cannot be explained by the charge effect and it is difficult to understand the mechanisms of P removal by different OH/Me ratio coagulants unless further investigations.

In this paper, simultaneous particle destabilization and P precipitation by most commonly used domestic WW treatment coagulants with different particle, P concentrations and OH/Al ratio of coagulant are discussed. The impact of particle removal mechanisms (charge neutralization – precipitation and sweep floc) and P precipitation mechanisms (formation of aluminum-hydroxy-phosphates complexes and direct adsorption) those may vary on the particle concentration, P concentration and OH/Al ratio of coagulant. The other chemical and physical processes which occur during coagulation will not be discussed.

## Materials and methods

Experiments carried out with model wastewaters. Compositions of synthetic wastewaters differed by phosphorous

and suspended solid contents. The exact compositions of model wastewaters are given in the Table 1.

The used coagulants were Kemira ALS (aluminum sulfate), Kemira PAX -18 and Kemira PAX –XL 61 (prepolymerized aluminum coagulants). We have also used an organic cationic polymer from SNF Floerger FO-4350, in a working solution of 1 g/l aquatic solution. The range of coagulant dosage variation included doses that were lower and higher than the optimum dose for each of the coagulants. In total, for each coagulant five dosages were used. The optimum doses were determined in the preliminary jar-test experiments.

Pre-coagulation experiments were carried out with each coagulant and in each dosage to find the initial pH to obtain final required pH. Moreover, in the pre-experiments pH vs. mg Al/l curves were developed to every 0.5 pH variation in the range of pH 7–10. These curves were used in real experiments to adjust initial pH of raw water to obtain coagulation pH of 7.5. Additionally to pH curves of only inorganic coagulants, pre-experiments were carried out for simultaneous and MIX dosing types of cationic polymer and developed separate pH curves. For the real experiments of coagulation process to reach coagulation pH in the desired pH value, the initial pH of raw water was adjusted according to the pH curves developed in the pre-experiments. Each experiment was carried out with three replicates to reduce uncertainties. In most cases, the jar-test coagulation experiments were carried out on the final coagulation mean pH value of  $(7.5 \pm 0.2)$ .

For the coagulation experiments, jar-test apparatus [22] was used with 1 L standard six beakers. The mode of mixing was: rapid mixing for 30 seconds, then slow mixing during 10 min followed by 15 min of sedimentation.

Two sets of experiments were carried out. First set of coagulations experiments were carried out as follows. Defined dosages of each coagulant were added to the jars at the beginning of the rapid mixing and then followed the automatic mode of mixing and sedimentation as mentioned above. After sedimentation, about 200 ml of supernatant was collected and used as a sample for further analysis.

For each supernatant sample, parameters such as SS, total phosphorous (TP), orthophosphates (OP) and turbidity were analyzed. Determination of SS content was done by gravimetric method. TP and OP contents were

**Table 1.** Composition of syntactic wastewater in mg/l.

mg/l	Water types for set 1 experiments						Water types for set 2 experiments					
	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10	Type 11	Type 12
SS (mg/l)	Constant			High	Medium	Low	Zero			High	Medium	Low
TP (mg/l)	High	Medium	Low	Constant			High	Medium	Low	Zero		

measured according to standard method ISO 6867/2004. Randomly selected samples were analyzed for the second time for TP and OP by Hach Lange LCK (349 and 350) chemical cuvettes and Hach DR 3900 spectrophotometer for accuracy and to reduce the human errors. Turbidity was measured by Hach 2100Q portable turbidimeter. The extents of SS removal and TP removal were the main parameters by which the evaluation of treatment efficiency was done.

The second set of experiments was carried out with model wastewaters; those were different from both with and without P and SS concentrations. Sludge or precipitant obtained after coagulation were analyzed for bonds of the coagulant-SS and coagulant-P. To obtain sludge from SS = 0 waters, it was used TP concentrations of 10, 20 and 30 mg/P l with Al dosages of 40 and 50 mg Al/l. Similarly, to obtain sludge without TP, model wastewater was prepared without TP and defined coagulant dosages were used.

Two types of dosing methods were used in the sludge analyzing experiments, simultaneous and dose-mix dose-mix (MIX) dosing of coagulant and polymer. While using simultaneous type of dosing, coagulant and cationic polymer were added simultaneously to the jars at the beginning of rapid mixing. At the MIX dosing type, there were two-30 seconds rapid mixing periods. Coagulant was added to the jars at the beginning of 1st rapid mixing and then polymer was added into the jars at the 2nd rapid mixing period. After sedimentation, supernatant was removed and collected about 200 ml of precipitant was used for further analysis. In addition to the sludge obtained by the both dosing types, sludge formed with only inorganic coagulant was also analyzed.

Formed precipitates were separated from the liquid phase by centrifuge, and then dried at 105°C until constant weight. At the first step, infrared (IR) spectroscopy analysis was used for the determination of the presence of aluminum – hydroxy and aluminum – P bonds in the dried sludge. The IR spectroscopy measurements were made on the Fourier Transform Infrared-Spectrometer: NEXUSTM E.S.P. (Thermo Nicolet, USA). The results showed that the samples obtained from the model water, containing P, were characterized by the presence of aluminum-hydroxyl complexes and aluminum-P in different ratio.

At the next step, the full quantitative and qualitative analysis of samples were done using Scanning Electron Microscope JSM-5610 LV with Energy Dispersive X-ray Spectrometer JED-2201JEOL (Japan). Using the results of quantitative and qualitative analysis the ratio of aluminum-hydroxyl complexes to aluminum-P was determined for each sample.

In order to reduce the number of required experiments while retaining the most important features,

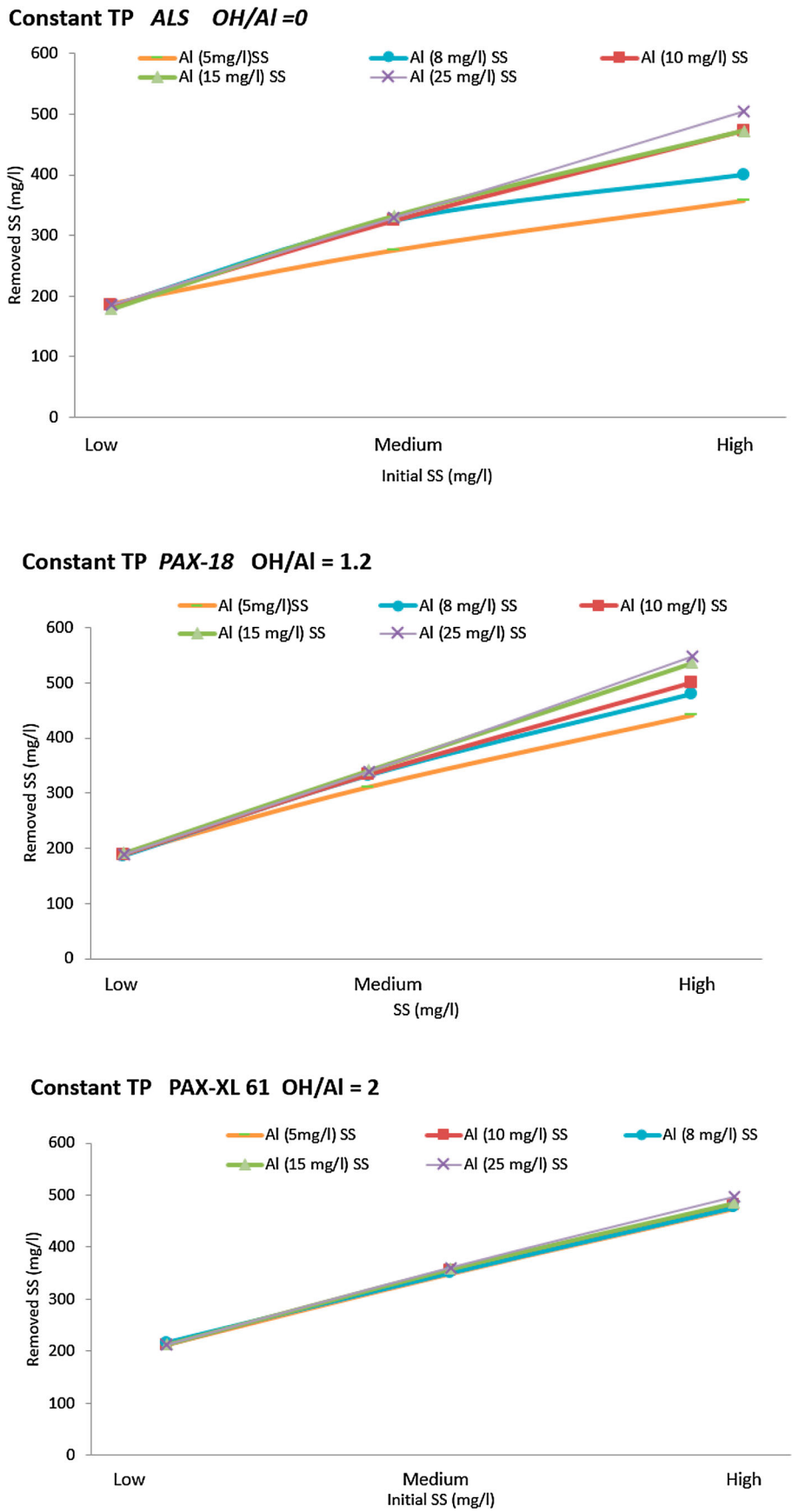
fractional factorial design of the experiment was made using UNSCRAMBLER X 10.2 software.

## Results and discussion

Experiments were carried out according to the experimental design. There was a noticeable difference between results obtained by different ratios of OH/Al in coagulant, levels of SS and TP in initial raw water while maintaining the same dosage of coagulant.

Figure 1 illustrates the relationship between initial SS concentration, coagulant dosage and OH/Al ratio for SS removal efficiencies at constant initial TP levels in synthetic wastewater (WW). Results show that SS removal at low initial SS concentration has no significant effect on OH/Al ratio nor the dosage of coagulant. For example, in all three coagulants, the removed amount of SS in low initial SS concentrations from 185 to 200 mg SS/l with dosages range of 5–25 mg Al/l were about 199–212 mg SS/l. According to schematic coagulation diagram of Stumm and O'Melia (1968), [23] this could be because the dosage and amount of SS are in the sweep-floc stage and/or near optimum coagulant dosages. The adsorption-charge neutralization (ACN) and sweep-floc mechanisms overlap. The critical coagulant concentration could be far beyond the  $\text{Al}(\text{OH})_3$  precipitation level; therefore there is no re-stabilization.

When in medium and high initial SS concentrations, the effect of coagulant dosage was significant in coagulants with OH/Al ratios 0 and 1.2, but coagulant with OH/Al ratio 2 has no effect at high or low initial concentration of SS. For example, difference between SS removal efficiency with dosage range from 5 to 25 mg Al/l of ALS was 150 mg SS/l and that with PAX-XL61 was 10 mg SS/l. This can be explained because at a higher ratio of OH/Al more  $\text{Al}(\text{OH})_3$  species are present in the system. These species trap or adsorb SS particles and precipitates (ACN). In a WW system with small dosages of higher OH/Al ratio, coagulants may precipitate completely all amounts of SS and the system has not enough SS to be removed with higher dosages. Therefore, the  $\text{Al}(\text{OH})_x$  could precipitate on their own or take part in other reactions in the system. In case of a system with extremely high concentration of SS and higher OH/Al ratio coagulant, there can be expected a significant effect of coagulant dosage on SS removal. Furthermore, if the coagulant with low OH/Al ratio is used, the main hydrolysis product will be  $\text{Al}(\text{OH})_3$  and the SS particles have less options for adsorption-precipitate than with coagulant with higher OH/Al ratio at the same dosage. A portion of Al in low ratio coagulant will be used for the formation of Al-hydroxo complexes and an additional amount of Al will be required for sufficient



**Figure 1** . Influence of initial concentration of SS, dose of Al and OH/Al ratio of coagulant on SS removal in synthetic wastewater with constant TP content at coagulation pH of 7.5.

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SS removal. Reason for the higher destabilization efficiency of  $\text{Me}(\text{OH})_x$  products in a coagulant with higher OH/Al ratio could be the polymeric nature and high charge character.

Figure 2 explains the relationship between initial SS concentration of WW versus removal efficiencies of OP and SS in water with constant initial TP level. According to the Figure 2, with the increase in initial SS concentration in raw water (maintaining constant TP level), the SS removal efficiency increases whereas OP removal efficiency decreases, for both coagulants and for all the studied dosages. When there are more particles compared with OP, the particles compete the P and distress the Me-P adsorption in both TP removal mechanisms of Al-hydroxo complex-P and  $\text{Al}(\text{OH})_x\text{-P}$ .

Samples were analyzed on scanning electron microscope with chemical microanalysis. WW types which were used in these experiments had zero TP and different SS concentrations with high and low OH/Al ratio coagulants. Sludge samples which were obtained after coagulation were analyzed for the percentage of Al  $(\text{OH})_x$ -complexes.

Figure 3 illustrates the percentage of Al atoms contained in sludge which present in all forms of Al. The sludge was obtained with different initial SS levels in raw wastewater and with different OH/Al ratio coagulants. There was a significant effect of OH/Al ratio of coagulant on formation of Al atoms in sludge. These Al-atoms could be a result of formation of  $\text{Al}(\text{OH})_x$ -complexes in coagulation stage. The proportion of Al in

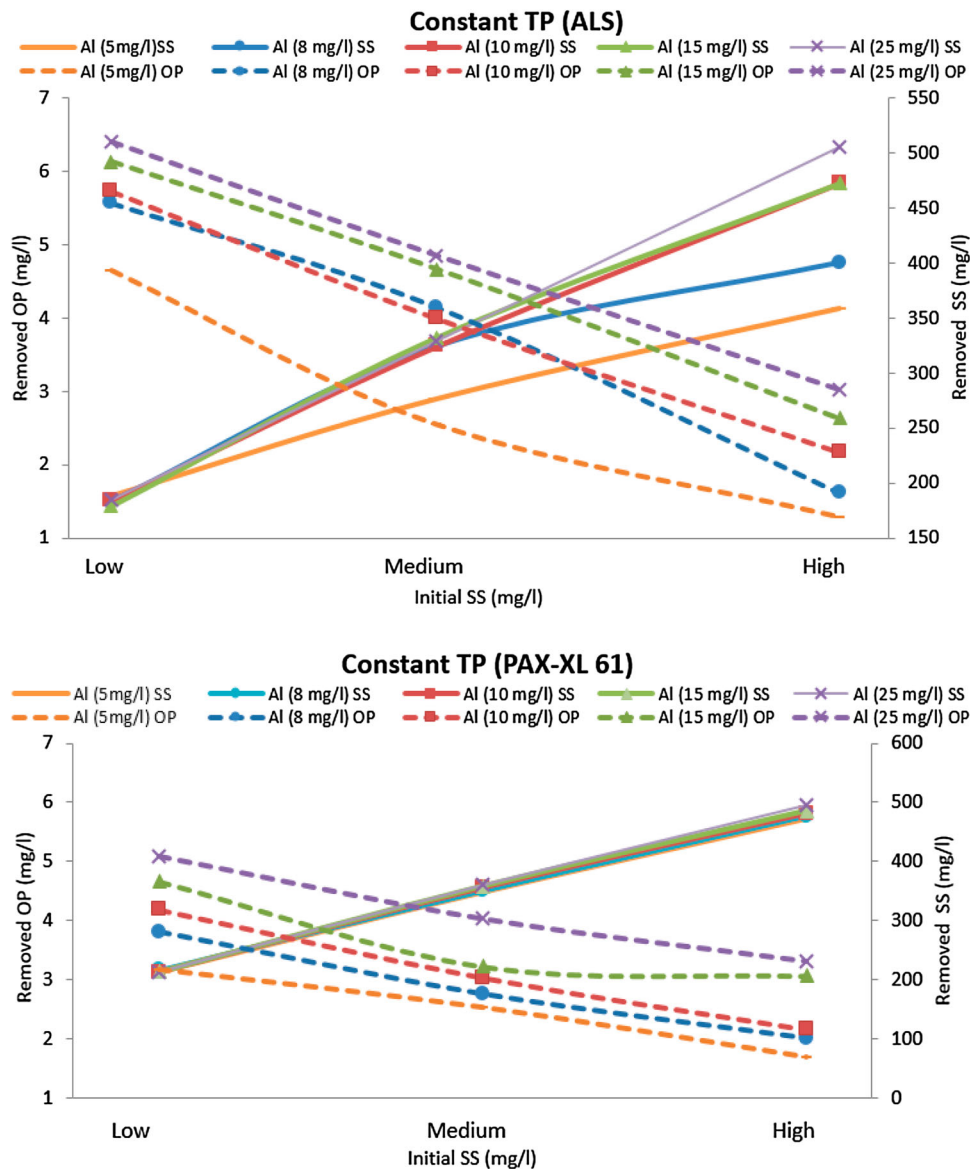
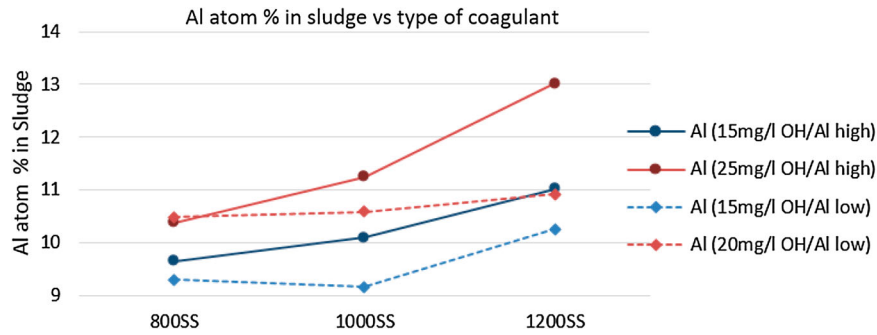


Figure 2. Influence of initial concentration of SS and Al dosage on removed mg/l of SS and OP in synthetic wastewater with constant initial TP concentration at coagulation pH of 7.5 (OH/Al low coagulant-ALS and OH/Al high coagulant-PAX-XL61).



**Figure 3.** Influence of type of coagulant (low and high OH/Al) and initial raw water SS concentration in formation of  $\text{Al}(\text{OH})_x$  complexes in the sludge.

form of complex formation in the sludge increased with the increase in OH/Al ratio of coagulant. In a coagulant with high OH/Al ratio, a great amount of the Al involves in hydrolysis with polymer at the coagulant pre-polymerized stage and these Al-hydrolysis-polymers or  $\text{Al}(\text{OH})_x$ -complexes have greater amount of SS-particles-adsorbing ability. In a coagulant with low OH/Al ratio, considerable amount of Al-ions is involved in inner reactions than it is with high-ratio coagulants. Moreover, the main hydrolysis product of lower ratio coagulant is  $\text{Al}(\text{OH})_3$ , which may have low ability for particle removal by sweep-floc mechanism than with the pre-polymerized coagulant.

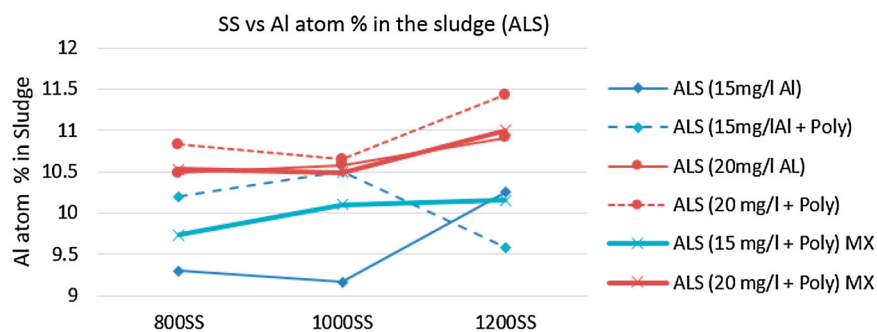
Figure 4 illustrates the results of qualitative analysis of sludge samples conducted by scanning electron microscopy with chemical microanalysis. As can be seen from Figure 4, with an increase in SS in raw water at the same coagulant (Al) dosage, the percentage of Al atoms in the form of  $\text{Al}(\text{OH})_x$ -complexes in the sludge also increased. Possible explanation is that when there are more particles, more  $\text{Al}(\text{OH})_x$  species adsorb/trap particles and precipitate them. Similar conclusions were mentioned in the discussion of the results represented by Figures 2 and 3.

Comparing dosing types, simultaneous dosing had higher effect on precipitating Al atoms in sludge than

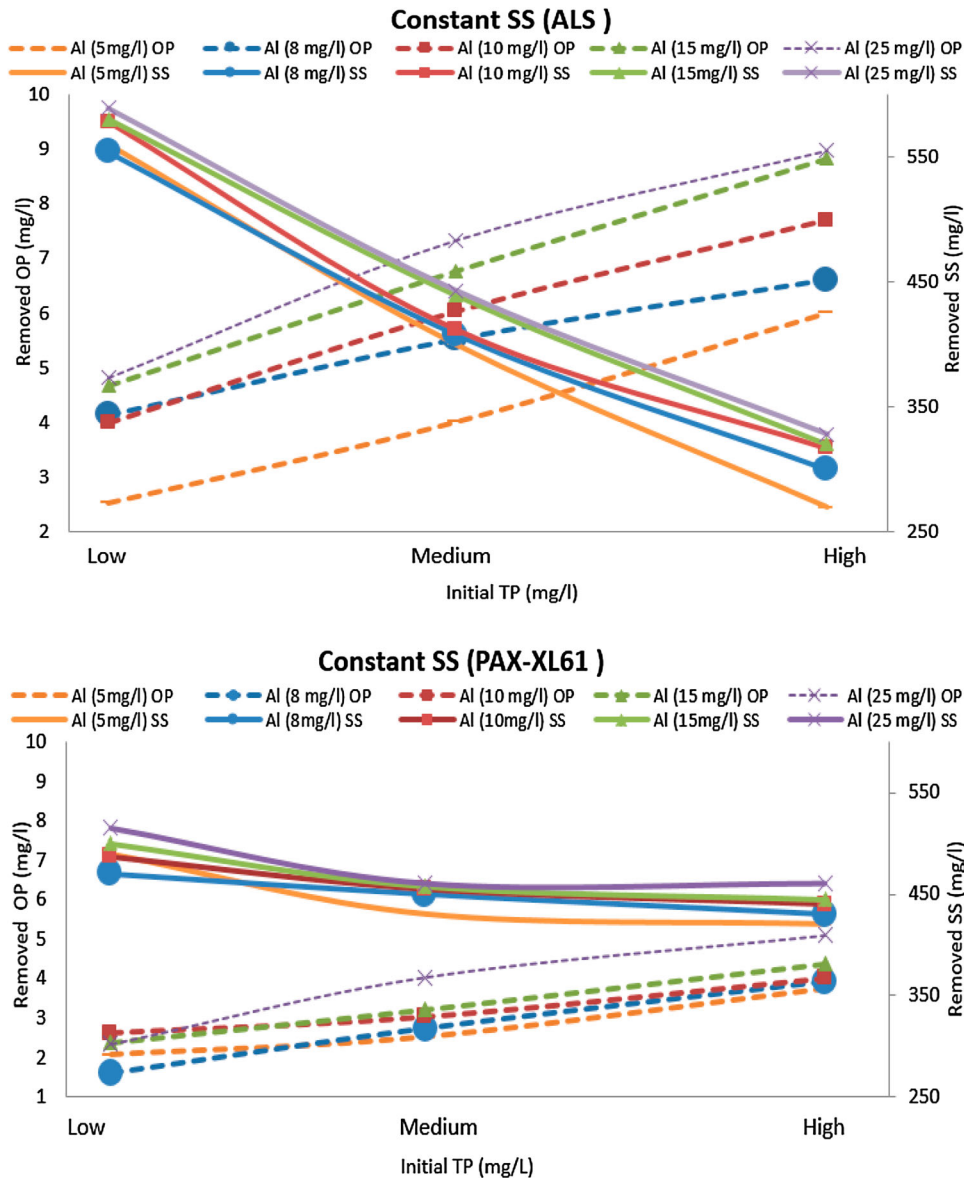
MIX dosing. This could be explained by the fact that at MIX dosing, flocs formed at the first mixing step were broken at the second mixing step, which prevented their precipitation during sedimentation stage.

If to compare TP removal efficiency with the OH/Al ratios of the coagulants, at constant initial SS concentration of the raw water, the phosphate removal efficiency changed in reverse proportion to OH/Al ratio of the coagulant (Figure 5). Similar results were proved and documented by many researchers. The mechanisms involved in P removal proposed in the literature are: (1) formation of Al-hydroxo-P complexes; (2) adsorption of P ions onto Al-OH<sub>x</sub>-complexes.[7,24] However, high OH/Al ratio in a coagulant makes the first mechanism prevailing, while low OH/Al ratio of a coagulant is more preferable for the occurrence of the second one. The extent of P removal at both mechanisms depends on OH/Al ratio of coagulant. Therefore, the coagulants with high OH/Al ratios predominantly form Al-hydrolysis species, which have low capacity for P-precipitate formation during the hydrolysis reaction than Al-hydroxo-P-complexes.

Figure 5 shows that removal efficiencies of TP were found to increase and SS removal efficiencies to decrease with the increase in the initial TP concentration at the constant initial SS concentration of raw water. The



**Figure 4.** Percentage of Al in form of  $\text{Al}(\text{OH})_x$  as a proportion of all Al contained in sludge samples obtained with the use of different coagulant dosages, dosing types simultaneous and add-mix-add-mix (MIX) and initial SS concentration in raw water.



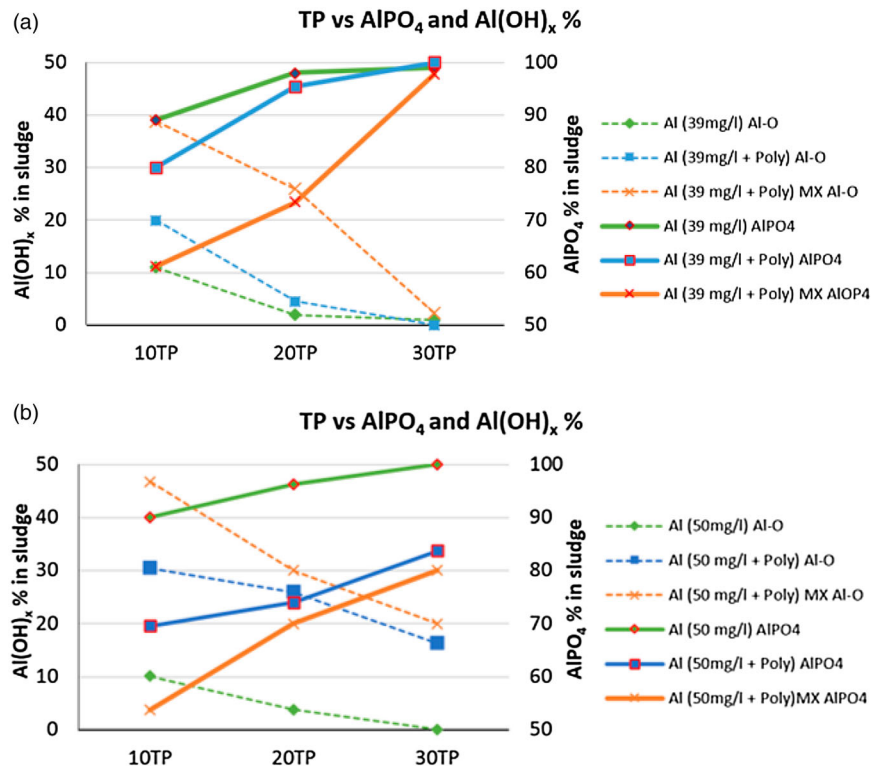
**Figure 5** . Impact of initial concentration of TP and Al dosage on SS and OP removal in synthetic wastewater with constant initial SS concentration at coagulation pH of 7.5 (OH/Al low coagulant-ALS and OH/Al high coagulant-PAX-XL61).

reactions of Al-P and Al-SS formation are competing, and when there were more SS, then Al-SS formation was dominant, and when there were more P, then Al-P formation dominated. This could be because SS particles' surfaces may cover the access of P to Me-ions and Me (OH)<sub>x</sub> species. Negatively charged, comparing large surfaces of SS could cover or adsorb the positively charged hydrolysis products and hinder P surfaces to adsorb Me ions or/and Me (OH)<sub>x</sub> species. Similarly, the opposite action could occur when there was greater amount of P than SS particles in the system.

Figure 6, illustrates the effect of initial TP concentration in raw water, coagulant dosage and dosing type on formation of AlPO<sub>4</sub> and Al(OH)<sub>x</sub>. It can be seen from Figure 6 that in the water with zero SS and different TP

levels, formation of AlPO<sub>4</sub> in the sludge increased with the increase of TP levels in raw water at same coagulant dosage. Opposite trend was observed in Al(OH)<sub>x</sub> formation. Collision theory states that in order for a reaction to occur, the reacting particles must collide. The number of collisions depends on the number of particles.[25] When there is more P in the system, more collisions/electro static reactions will occur between Al and P, while Al(OH)<sub>x</sub> formation reactions will drop down.

Furthermore, it can be clearly seen that in the both dosages in all three TP concentrations the formation of AlPO<sub>4</sub> in the sludge was lower at MIX dosing than at simultaneous dosing. For example, with 50 mg Al/l dosage at initial TP level of 10 mg TP/l the proportion of all Al contained in sludge in form of Al(OH)<sub>x</sub> was 53% at MIX dosing



**Figure 6.** Effect of coagulant dosage (A-low dosage and B-high dosage), dosing methods simultaneous and add-mix-add-mix (MIX) and initial raw water TP concentration in formation of  $\text{AlPO}_4$  and  $\text{Al}(\text{OH})_x$  in the sludge.

and it was 70% at simultaneous dosing. Similar trend was observed at 39 mg Al/l dose. This could be because at the first step of the MIX dosing when Al was added to the system, most of the Al from coagulant was consumed for creation Al-P as there was no SS in the system. At second step, when polymer was introduced to system, the formed Al-P complexes combine with polymer and made bigger flocs and precipitated. To discuss this more deeply, further investigation is required.

## Conclusions

Particle and phosphate removal are competitive reactions and the Al-hydrolysis reaction depends on particle concentration. When there are more SS the formation of  $\text{Al}(\text{OH})_x$  increases and SS removal efficiency increases and the opposite trend is observed for TP removal.

Similarly, increasing the phosphate concentration in the system with same SS level, the TP removal efficiency increases and SS removal decreases.

Simultaneous dosing of coagulant and polymer has higher removal efficiency of both TP and SS than the dosing method of add-mix-add-mix.

Phosphate removal depends on OH/Al ratio of coagulant. At low ratios, phosphates are removed dominantly by formation of Me-hydroxo-P-complexes, while at higher OH/Al ratios removal is made by  $\text{Me}(\text{OH})_x\text{-P}$ . Me-

hydroxo-P-complexes have higher capacity of phosphate removal than  $\text{Me}(\text{OH})_x\text{-P}$ .

## Disclosure statement

No potential conflict of interest was reported by the authors.

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