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Elisangela Heiderscheidt

EVALUATION AND OPTIMISATION OF CHEMICAL TREATMENT FOR NON-POINT SOURCE POLLUTION CONTROL

PURIFICATION OF PEAT EXTRACTION RUNOFF WATER

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU,
FACULTY OF TECHNOLOGY

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ELISANGELA HEIDERSCHEIDT

EVALUATION AND OPTIMISATION OF CHEMICAL TREATMENT FOR NON-POINT SOURCE POLLUTION CONTROL

Purification of peat extraction runoff water

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defence in Kuusamonsali (YB210), Linnanmaa, on 21 October 2016, at 12 noon

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Abstract

Chemical treatment is considered best available technology for purification of peat extraction runoff in Finland, due to its capability to remove dissolved organic carbon (DOC), suspended solids and nutrients. However, lack of optimisation and adaptation of this method for purification of diffuse pollution sources, e.g., peat extraction runoff, has led to significant fluctuations in purification efficiency. This thesis evaluated the suitability of commercially available coagulants for the treatment of typically humic water. Inorganic (ferric sulphate, aluminium sulphate and a mixed product) and organic (polyDADMAC, polyamine, chitosan and tannin products) coagulants were studied. Investigations included assessment of required dosage and the influence of process parameters (pollutant concentration, mixing, water pH and temperature) on coagulant performance. In addition, the process conditions in existing treatment systems were examined in field experiments aimed at identifying possible factors affecting purification.

Ferric sulphate (FS) was the most effective of the coagulants tested. It produced excellent flocs and achieved higher removal efficiency, particularly for DOC, than the other coagulants. However, the dosage required for FS was significantly higher than for e.g., polyDADMAC and chitosan. Moreover, samples treated with FS displayed high iron concentration and acidic pH. The organic polymers achieved satisfactory results, but further research is needed before they can become viable alternatives to metal salts.

The quality of peat extraction runoff water was found to vary significantly. It was also observed that variations in DOC concentration, even for particulate rich samples, controlled coagulant dosage and, consequently, treatment efficiency. For inorganic coagulants, mixing provided during flocculation had a more significant influence on purification than mixing provided during coagulation. This is relevant hence in now existing treatment facilities no mixing is employed during flocculation. Based on the research conducted, suggestions were formulated for process optimisation aimed at reducing variations in purification efficiency, thus increasing the reliability of the method and reducing related environmental impacts.

Keywords: DOC removal, ferric sulphate, organic coagulants, peat extraction, water quality

Heiderscheidt, Elisangela, Kemiallisen käsittelyn toimivuuden arviointi ja optimointi hajakuormituksen hallintaan. Turvetuotannon valumavesien puhdistus

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Tiivistelmä

Turvetuotannon valumavesien käsittelyssä yksi parhaista käyttökelpoisistatekniikoista on kemiallinen käsittely, koska se pystyy poistamaan valumavedestä liukoista orgaanista hiiltä (DOC), kiintoainetta ja ravinteita. Tästä huolimatta kemiallisen käsittelyn optimointia ei ole tehty hajakuormitukselle, kuten turvetuotannon valumavesille, minkä seurauksena valumavesien puhdistustuloksissa on suurta vaihtelua. Tässä väitöstyössä tutkittiin markkinoilla saatavilla olevien kemikaalien sopivuutta turvetuotannon humuspitoisille valumavesille. Tutkimuksessa testattiin epäorgaanisia (ferrisulfaatti, alumiinisulfaatti ja näiden sekoitus) ja orgaanisia (polyDADMAC, polyamiini, kitosaani ja tanniinipohjaisia polymeerejä) koagulanttikemikaaleja. Tutkimuksessa selvitettiin koagulanttien annostarpeet sekä erilaisten prosessiparametrien (vedenlaatu, sekoittaminen, pH ja lämpötila) vaikutus koagulanttien toimintaan. Laboratoriotutkimusten lisäksi väitöstyö sisälsi kenttämittauksia turvetuotannon valumavesien tyypillisten kemiallisen vesienkäsittelyn prosessiparametrien selvittämiseksi.

Tutkituista koagulanteista rautasulfaatti oli tehokkain. Se tuotti hyvin laskeutuvaa flokkia ja poisti parhaiten valumavesien orgaanista ainesta. Rautasulfaatti vaati kuitenkin selkeästi suuremman annostuksen kuin esimerkiksi polyDADMAC ja kitosaani. Lisäksi puhdistettuun veteen jäi paljon rautaa ja vesi oli hapanta. Orgaanisilla kemikaaleilla saavutettiin myös kohtalainen/melko hyvä puhdistustulos, mutta lisää tutkimusta tarvitaan ennen kuin ne voivat olla vaihtoehtona epäorgaanisille kemikaaleille.

Turvetuotannon valumaveden laatu vaihteli paljon. Valumaveden orgaanisen aineen määrän vaihtelulla oli suurin vaikutus kemikaalin annostukseen ja puhdistustulokseen. Sekoituksista kemiallisen käsittelyn flokkulaatiovaiheen sekoituksella oli suurempi vaikutus puhdistustulokseen kuin koagulaatiovaiheen sekoituksella. Tutkituilla turvetuotantoalueilla ei kuitenkaan ollut tällä hetkellä riittävää sekoitusta flokkulaatiovaiheessa. Tässä väitöstyössä esitetään parannuksia kemiallisen käsittelyn optimointiin paremman ja vakaamman puhdistustuloksen aikaansaamiseksi humuspitoisille vesille.

Asiasanat: DOC:n poisto, orgaaninen koagulantti, rautasulfaatti, turvetuotanto, veden laatu

To my family, especially my lovely son and wife and in memory of my father, whom I miss dearly

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Abbreviations

abs.	Absorbance
Alk	Alkalinity
Alum	Aluminium sulphate
ANOVA	Analysis of variance
BAT	Best available technology
CD	Charge density
CFD	Computational fluid dynamic
Chit	Chitosan
COD	Chemical oxygen demand
Cq	Charge quantity
DOC	Dissolved organic carbon
EC	Electric conductivity
eq/L	Equivalents per litre
FS	Ferric sulphate
HS	Humic substances
LC	Liquid chromatography
MW	Molecular weight
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
OC	Orthogonal contrast
OCD	Organic carbon detection
OND	Organic nitrogen detection
pAmine	Epichlorohydrin-dimethylamine copolymer
pd	Pre-dissolved
pDMAC	Poly(diallyldimethyl) ammonium chloride
rpm	revolution per minute
sol	Solid
SS	Suspended solids
SUVA	Specific UV absorbance
Tan	Tannin-based polymer
TOC	Total organic carbon
tot-N	Total nitrogen
tot-P	Total phosphorus
UV	Ultraviolet

Original publications

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:

I Heiderscheidt E., Saukkoriipi J.T., Ronkanen A-K., Klöve B., 2013. Optimisation of chemical purification conditions for direct application of solid metal salt coagulants: Treatment of peatland-derived diffuse runoff. Journal of Environmental Sciences 25(4), 659–669.
DOI:10.1016/S1001-0742(12)60111-9

II Heiderscheidt E., Leiviskä T., Ronkanen A-K., Kløve B., 2016. Evaluating the suitability of synthetic organic polymers to replace iron salts in the purification of humic and sediment-rich runoff. Desalination and Water Treatment 57 (23), 10948–10957.
DOI:10.1080/19443994.2015.1043954

III Heiderscheidt E., Leiviskä T., Kløve B., 2016. Coagulation of humic waters for diffused pollution control and the influence of coagulant type on DOC fractions removed. Journal of Environmental Management (*in press*).
DOI:10.1016/j.jenvman.2016.06.043

IV Heiderscheidt E., Leiviskä T., Kløve B., 2015. Chemical treatment response to variations in non-point pollution water quality: results of a factorial design experiment. Journal of Environmental Management 150, 164–172.
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The author's contributions to publications I–IV was as follows:

I Elaborated the research plan together with Jaakko Saukkoriipi, performed the laboratory experiments, analysed the results and wrote the paper. Jaakko Saukkoriipi, Anna-Kaisa Ronkanen and Bjørn Kløve critically commented on all versions of the manuscript.

II Elaborated the research plan together with Anna-Kaisa Ronkanen, performed the laboratory experiments, analysed the results and wrote the paper. Tina Leiviskä, Anna-Kaisa Ronkanen and Bjørn Kløve critically commented on all versions of the manuscript.

III Elaborated the research plan together with Tina Leiviskä, performed the laboratory experiments, analysed the results and wrote the paper with inputs from Tina Leiviskä. Bjørn Kløve critically commented on all versions of the manuscript.

IV Elaborated the research plan together with Bjørn Kløve, performed the laboratory experiments, analysed the results and wrote the paper. Tina Leiviskä and Bjørn Kløve critically commented on all versions of the manuscript.

Contents

1 Introduction

Over recent decades, great efforts have been devoted to improving the quality of surface water and groundwater sources in Europe. The impact of pollution from land use activities such as agriculture, forestry and mining has been recognised and policies have been adopted in a number of countries, with the objective of meeting the requirements of the European Water Framework Directive (European Commission, 2015).

Peatlands cover around 9.3 million ha of Finland's surface area (30%) and, although 1.2 million ha are technically suitable for peat extraction, less than 1% of the total peatland area is exploited, mainly for energy production (90%) (Finnish Ministry of the Environment, 2015). Nevertheless, peat extraction causes a series of negative impacts on the environment, which can be significant at local scale, with the most severe impacts being those imposed on water sources (Kettunen *et al.*, 2012; Finnish Ministry of the Environment, 2015). Tightening of environmental legislation and increased awareness of environmental issues within the peat extraction industry have led to optimisation of existing water protection measures and the development of innovative solutions to reduce the contaminant load from peat extraction areas.

1.1 Peat extraction and its influence on water quality

Activities connected to peat extraction, such as peatland drainage and the exposure of peat layers, are known to increase the amount of water discharging from catchment areas (Holden et al., 2006) and also to increase the transport of pollutant substances such as suspended solids (SS), dissolved organic carbon (DOC), metals and nutrients into water courses located downstream (Heikkinen, 1990; Heikkinen, 1994; Kløve, 2001; Marttila and Kløve, 2008). Prediction of the contaminant load imposed by different land use activities is a difficult task due to e.g. temporal and spatial fluctuations in pollutant concentrations (Heathwaite, 1999). In the case of peat extraction, significant fluctuations in pollutant concentrations have been observed at monitored sites (Svahnbäck, 2007). The load dependence has been linked to drainage intensity, soil geochemistry and runoff rate (Edén *et al.*, 1999; Åström *et al.*, 2001, Kløve, 2001; Worrall *et al.*, 2003; Marttila and Kløve, 2008; Tuukkanen *et al.*, 2014).

Among the possible impacts caused by increased loading resulting from peat extraction activities are those related to higher concentrations of nutrients, SS and

DOC in aquatic environments. In Finland, an increasing trend in DOC concentrations has been observed in rivers and lakes (Vuorenmaa *et al.*, 2006). High organic load in lakes can result in oxygen depletion due to higher oxygen consumption, especially during incomplete spring turnover or long winters (Keskitalo *et al.*, 1999). De-oxygenation can cause internal eutrophication and can have a significant impact, e.g. on fish populations in the receiving water bodies (Evans et al., 2005). Higher DOC concentrations not only affect the aquatic ecosystem, but also the treatability of the water (Worrall and Burt, 2009). In potable water production, higher DOC concentrations are known e.g. to increase chemical demand during the coagulation/flocculation stage, cause fouling of membranes and activated carbon filters, and also to increase the formation of disinfection by-products etc. (Sillanpää, 2015). Higher particulate and nutrient loads, in particular of phosphorus, are also cause for concern, especially in regions of sensitive freshwater systems. Phosphorus is often the growth-limiting factor for plants and microorganisms in rivers and lakes in Finland (Lamon *et al.*, 2008) and, together with deposition of SS, is the main factor causing eutrophication, siltation and water quality deterioration (Finnish Ministry of the Environment, 2015).

1.2 Water purification methods in peat extraction

The peat extraction industry operates under strict environmental controls in Finland. Water protection measures are defined in environmental permits issued by the Finnish environmental authorities on a site-by-site basis (Finnish Ministry of the Environment, 2015). However, there are wide variations in runoff water quality with time, location and peak discharge occurrence (Kløve, 2001; Svahnbäck, 2007; Marttila and Kløve, 2008; Tuukkanen *et al.*, 2014), which represents a challenge in selection of adequate water purification methods. It is important to note that different sites will require different treatment methods designed to satisfy the requirements of the peat production process, site hydrology and geology, the sensitivity of the receiving water bodies and current legislation.

A number of water purification methods have been developed or adapted to the conditions prevailing at peat extraction sites, with the objective of reducing the pollutant loads from this land use activity (Kløve, 2001; Turveteollisuusliitto, 2010). In these methods, existing drainage networks are generally used to direct the flow of runoff water. Load retention measures are then applied within the ditch network or at its end point, in a main ditch or channel into which the network discharges. In the early days, treatment methods referred to as basic methods were used in Finland, e.g. sedimentation ponds and peak runoff control dams. However, with the tightening of the environmental legislation, additional treatment steps referred to as enhanced treatment methods are now required at most sites. Such enhanced treatment methods include overland flow fields (wetland) and chemical purification. The most widely used basic and enhanced treatment methods at Finnish peat extraction sites are (Turveteollisuusliitto, 2010):

i. Constructed sedimentation pond (Fig. 1a). It consists of a pond excavated in the proximity of the peat extraction area into which the runoff water is discharged. The retention time is designed to allow the removal of SS and associated nutrients from the water. Under normal discharge conditions, 40% removal of SS can be expected (Turveteollisuusliitto, 2010).

ii. Peak runoff control dam (Fig. 1b). It consists of a weir structure that controls the volume of water discharging from a ditch or channel. While controlling water discharge rates, this structure also traps peat particles, eroded substances and nutrients, as well as acting as an auxiliary in ditch erosion reduction. Marttila and Kløve (2009) report the following load reductions for peak runoff control dams: 61–94% for SS, 45–91% for total nitrogen (tot-N) and 47–88% for total phosphorus (tot-P).

iii. Overland flow field (treatment wetlands or constructed wetlands) (Fig. 1c). This involves directing the runoff water into the surface layer of a pristine or previously drained peatland area. The vegetation of the surface layer works as a mechanical filter, separating out solids from the water. Dissolved nutrients are removed in the peat layer as a result of chemical and biological processes. Average SS removal is around 60%, while around 25% of tot-N and tot-P is retained (Pöyry, 2014). The overland flow field is considered best available technology (BAT) for the purification of peat extraction runoff by the Finnish environmental authorities and is the most widely applied load reduction measure.

iv. Chemical purification (Fig. 1d). The chemical treatment method involves addition of coagulant agents normally used in water and wastewater treatment into runoff water discharging from the main ditch. The water is then directed to a sedimentation pond (see section 1.3.3). The addition of coagulation chemicals causes precipitation and

> sedimentation of solids and dissolved substances, which are deposited in the bottom of the sedimentation pond. Expected load reduction levels are: 30–90% of SS; 30–60% of tot-N and 75–95% of tot-P (Turveteollisuusliitto, 2010). Chemical treatment is also considered BAT for peat extraction runoff in Finland.

Due to their low maintenance requirement and natural credentials, wetlands are the most widely applied enhanced purification method. For example, the major Finnish peat extraction company Vapo Oy has built over 500 wetlands and only around 25 chemical treatment systems at its extraction sites since the late 1990s, when enhanced treatment methods started to be required by the environmental authorities (Wichmann, 2015)

Although purification requirements are set by authorities on a case-by-case basis, guidelines released by the Finnish Ministry of the Environment (2015) state that the removal efficiency to be achieved by treatment methods applied in conjunction with sedimentation ponds (mostly wetlands) should be: 50% of SS, 40-50% of tot-P and 20% of tot-N. Requirements for organic matter removal are normally not imposed, since it is generally recognised that wetlands are not capable of effectively removing organic substances (Pöyry, 2014). According to Vapo Oy (Wichmann, 2015), the pollutant removal rates imposed by the authorities via environmental permits for sites where chemical purification is required are higher than those imposed at other sites. On a site-by-site basis, the removal rates required from chemical purification are: 60–80% removal for chemical oxygen demand (COD), 60–90% for tot-P, 30–50% for tot-N and around 50% for SS.

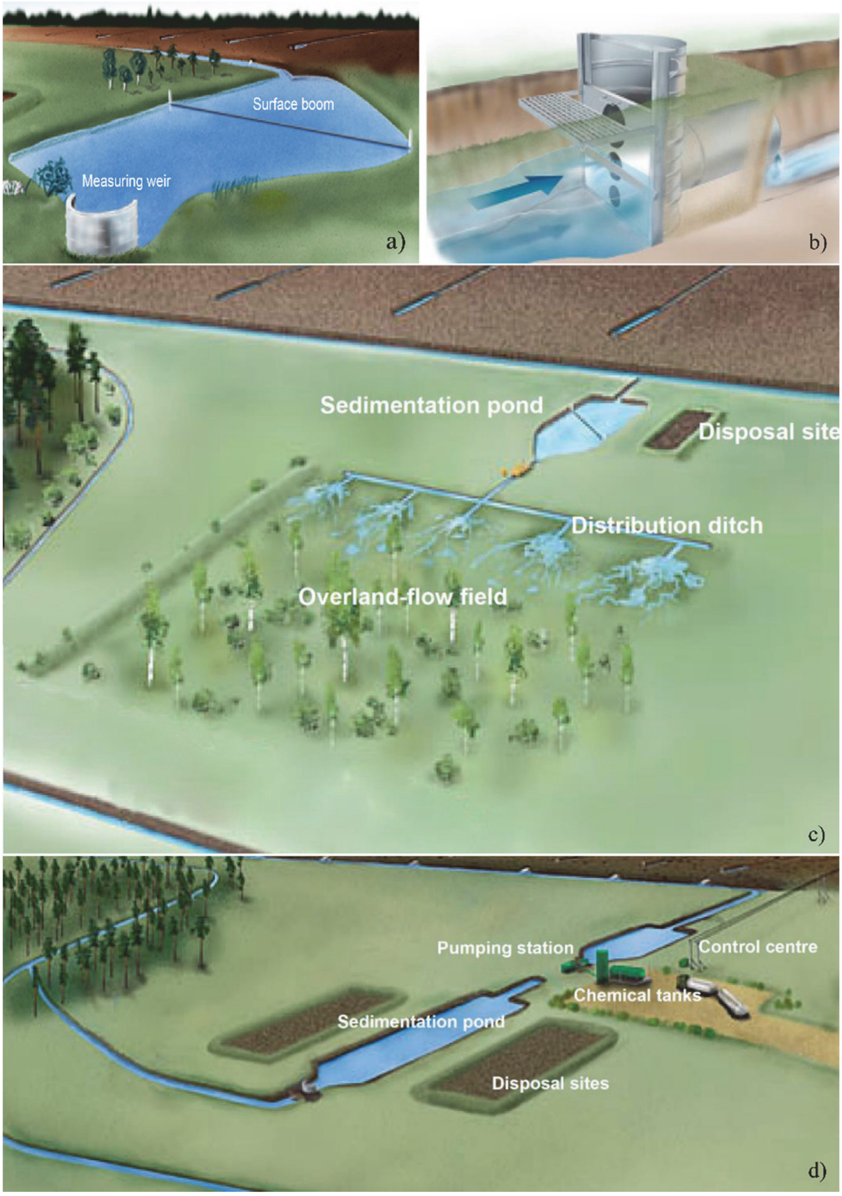


Fig. 1. The most commonly used water purification methods for peat extraction areas in Finland. a) Constructed sedimentation pond, b) peak runoff control dam, c) overland flow field and d) chemical purification (Revised and reprinted with permission from Turveteollisuusliitto, 2010).

1.3 Chemical purification

Natural sedimentation can easily remove larger suspended particles present in water. However, dissolved substances and very fine particles or colloids cannot be removed by sedimentation alone and their removal is the main objective of chemical treatment (Koohestanian *et al*., 2008). Chemical purification by addition of coagulation and flocculation chemicals is widely used for the treatment of water and wastewater all over the world. The method consists of two individual but well-interconnected and somewhat overlapping processes, coagulation and flocculation, followed by a solid-liquid separation phase, e.g. sedimentation (Bratby, 2006).

1.3.1 General aspects of chemical purification

Coagulation is a chemically induced destabilisation process in colloidal systems involving addition of counter-ions to the charges contained in the solution or suspension (Bratby, 2006). In natural waters, due to their acidic nature, most substances are negatively charged and therefore they repel each other and remain dispersed in the liquid. During chemical purification, counter-ions are introduced by addition of chemicals referred to as coagulants (or primary coagulants), which have the ability to precipitate SS and dissolved substances present in the water, forming primary particles (Gregory and Duan, 2001; Duan and Gregory, 2003; Bratby, 2006; Bolto and Gregory, 2007). Flocculation is the agglomeration of particles due to induced fluid motion. By inducing gentle motion and creating velocity gradients within the water, the primary particles formed during coagulation are encouraged to make contact and form larger agglomerates referred to as flocs (Bratby, 2006). These larger particles can then be easily removed by a solid liquid separation process such as sedimentation or flotation. Flocculants are chemicals (normally organic polymers) added to help the destabilisation process and accelerate the rate of flocculation or to strengthen the flocs formed (Bratby, 2006).

The efficiency of chemical treatment is known to be strongly dependent on water quality characteristics such as temperature, alkalinity, pH and the concentration and type of pollutant substances (e.g. Volk *et al*., 2000; Franceschi *et al*., 2002; Sharp *et al*., 2006; Xiao *et al*., 2008; Slavik *et al*., 2012). Furthermore, process parameters such as coagulant/flocculant type and dosage (e.g. Guibal *et al*., 2006; Liu and Chin, 2009; Wei *et al*., 2009; Libecki, 2010) and mixing during and after chemical addition (Yan *et al*., 2009; Zhan *et al*., 2011; Slavik *et al*., 2012) are known to have a significant impact on the results obtained. Several complex interactions occur between substances present in the water, added chemicals and other process parameters (inclusion of mixing, retention time etc.). Optimum purification conditions are generally water- and coagulant/flocculant agent-specific and are normally identified using the jar test and/or other pilot test methods (Bratby, 2006).

1.3.2 Coagulation and flocculation chemicals

Due to their effectiveness, availability and low cost, metal salts of iron and aluminium (sulphate and chloride as counter-ions) are the most commonly used primary coagulants in water and wastewater treatment all over the world. When metal salts are added to water, they dissociate and undergo a series of metal-ion hydrolysis reactions. The species produced and their characteristics are significantly dependent on dosage, mixing and water pH (Gregory and Duan, 2001; Duan and Gregory, 2003; Bratby, 2006). The efficacy of these inorganic coagulants is related to their ability to form multi-charged polynuclear species with high adsorption capacity and an amorphous precipitate (Bratby, 2006). Pre-hydrolysed metal salt coagulants have been developed by controlled metal-ion hydrolysis reactions, with the objective of producing the most effective species for destabilisation irrespective of process conditions. Pre-hydrolysed salts have been found to be required in lower doses and to be less sensitive to the pH and temperature of the water (Cheng, 2002; Jiang and Wang, 2009; Liu and Chin, 2009).

Synthetic organic polymers have been employed for decades in the treatment of water and wastewater, as flocculants and sludge dewatering chemicals (Bolto, 1999; Bratby, 2006; Gregory and Bolto, 2007). Although their use as primary coagulants is not widespread, it is expected to increase as the technology for their production advances and tailor-made products with varying molecular weight (MW), charge density (CD) and lower residual monomers are produced (Gregory and Bolto, 2007). For example, cationic polymers such as poly(diallyldimethyl) ammonium chloride (pDMAC) with high CD have been successfully applied as primary coagulants in water treatment (Nozaic *et al.*, 2001). Some advantages of synthetic organic polymers over metal salt coagulants are that they do not consume alkalinity, have been found to display lower sensitivity to variations in water quality, require lower dosages and produce less sludge with better dewatering characteristics (Nozaic *et al.*, 2001; Gregory and Bolto, 2007). However, some concerns have arisen regarding their low degradability, high costs and toxicity, with potential harmful impacts on human health (Letterman and Pero, 1990) and on aquatic ecosystems (Harford *et al.*, 2011).

The need for less toxic and more environmentally friendly water treatment products has directed research into naturally produced polymers (biopolymers). Biopolymers are extracted from animals, plant tissues or microorganisms and have benefits such as non-toxicity and high biodegradability (Gregory and Bolto, 2007; Yin, 2010; Oladoja, 2015). Among the currently developed and commercially available biopolymers are chitosan and tannin-based products. Chitosan is produced from chitin, a biopolymer extracted from shellfish sources, and it is virtually insoluble in water under neutral conditions, but it can be dissolved in acid solutions such as acetic and hydrochloric acid (Renault *et al.*, 2009). Water-soluble modified chitosan polymers have been developed by e.g. controlled deacetylation and chemical modification methods (Kurita, 1991; Holme and Perlin, 1997). Several studies have evaluated the use of chitosan for the removal of turbidity and natural organic matter (NOM) (Bratskaya *et al.*, 2004; Guibal *et al.*, 2006; Renault *et al.*, 2009; Yang *et al.*, 2011; Chen *et al.*, 2015). Overall, they report advantages such as lower required dosage, lower metal residuals and lower (less toxic) sludge production compared with metal salts (Guibal *et al.*, 2006; Renault *et al.*, 2009; Chen *et al.*, 2015). Tannin is a general name given to large polyphenol compounds obtained from natural materials, such as organic extracts from tree bark and wood. Tannin-based coagulants have also been successfully tested for turbidity and organic matter removal (Graham *et al.*, 2008; Sánchez-Martín *et al.*, 2010).

1.3.3 Chemical purification of peat extraction runoff water

In the purification of peat extraction runoff water, chemical treatment is mostly employed at sites surrounded by sensitive ecosystems, where high removal rates are required, or at sites where suitable space for wetlands is not available. Metal salts of iron (sulphate as counter-ion) are the coagulant agents normally applied. The limiting factor for their application is generally the higher cost of implementation and maintenance and the higher need for process control compared with other purification measures (Turveteollisuusliitto, 2010; Finnish Ministry of the Environment, 2015; Finnish Environmental Institute, 2015). Furthermore, technical issues such as freezing of liquid coagulants during cold periods can result in seasonal application of the method (Turveteollisuusliitto, 2010).

Cost effectiveness is a significant problem for chemical purification of diffuse pollution. Implementation of treatment facilities where effective control of e.g.

retention time, dosage and mixing is accomplished is mostly not economically viable. Therefore, the method is implemented in a simple configuration with a low number of equipment and steps involved (Turveteollisuusliitto, 2010) (Fig. 1d). There are two types of chemical treatment system used in peat extraction sites, which are referred to as '*small-scale treatment units*' and simply '*treatment units*'. Small-scale treatment units are generally implemented at extraction sites smaller than 150 ha, while treatment units are implemented at larger sites. This is mostly due to cost-related issues (Finnish Ministry of the Environment, 2015). In small-scale units, solid metal coagulants are applied. At small-scale sites, electricity may not be available and thus dosing of the coagulant occurs by passive means and water flows by gravity from the main ditch into the sedimentation basin. When electricity is available, solid coagulants are added using a mechanical auger dosing system and the runoff water is transferred from the main ditch to the sedimentation basin by pumping. In treatment units, liquid coagulant products are applied using a dosing pump and the runoff water is transferred by pumping to the sedimentation basin (Finnish Ministry of the Environment, 2015). In both types of chemical treatment units, the dosage is kept constant during the whole operating period. The total costs of implementation and maintenance of small-scale treatment facilities using solid coagulants are reported to be 50–75% lower than for facilities using liquid coagulants (Alatalo and Peronius, 2004; Turveteollisuusliitto, 2010). Solid coagulants are cheaper and require less and simpler dosing equipment, and consequently fewer maintenance working hours, than liquid coagulants.

The simple configuration in which chemical purification is applied, combined with the lack of optimisation and adaptation of the method to the specific condition of non-point source pollution control (including variations in runoff water quality, temperature and discharge) has led to significant fluctuations in purification efficiency and to increased acidity, metal and sulphate concentration in the purified water (Finnish Ministry of the Environment, 2015; Finnish Environmental Institute, 2015). Under these conditions, chemical treatment can impose further impacts on receiving water bodies. For example, in addition to containing substances initially present in the runoff (nutrients, SS etc.), the discharging waters can also contain high residual concentrations of added coagulants, causing further deterioration in water quality. For example, high iron concentrations and acidic conditions have been found to have a significant impact on the structure and function of aquatic ecosystems (Vuori, 1995; Edèn *et al.*, 1999). There is thus an urgent need for solutions that can enable the purification process to better cope with existing conditions, while also decreasing performance variability and the negative environmental impacts associated with existing chemical treatment systems.

1.4 SULKA project

The SULKA (New and innovative methods of water purification to reduce loading from peat extraction) research project ran from 2011 to 2014, with a budget of around 1 million Euros. The project was mainly funded by Vapo Oy and was implemented by the Water Resources and Environmental Engineering research group (University of Oulu) in partnership with the Finish Environmental Institute – SYKE. Vapo Oy is the world's leading supplier of peat. The company is owned jointly by the Finnish state (50.1%) and Suomen Energiavarat Oy, a consortium of Finnish energy companies (49.9%).

The main objectives of the SULKA project were: i) to increase available knowledge regarding load formation and transport in peat extraction areas; ii) to identify suitable preventive measures to reduce load discharge; iii) to evaluate factors affecting purification efficiency in treatment wetlands; and iv) to identify factors affecting the chemical purification process. The overall aim was to develop solutions to minimise the inconsistency in purification results, while also increasing the cost-effectiveness.

The majority of the studies on which this thesis is based (Papers I–IV and background studies) were part of the SULKA project research. A summary of all results obtained in the project can be found in the final report (Finnish Environmental Institute, 2015). Additional investigations (e.g. that described in III) were planned and executed to expand the knowledge obtained within the project tasks.

1.5 Objectives

The focus of this thesis work was evaluation and optimisation of the chemical purification process for the purification of non-point source pollution, specifically for the treatment of peat extraction runoff water. The main goal was to gain new knowledge about the significance of process parameters and water quality characteristics for the purification efficiency achieved under field or real conditions. The work involved studying the applicability and reproducibility of the method for purifying runoff with varying water quality characteristics and developing tools and guidelines for the optimisation and effective use of this pollution control measure in order to decrease variations in purification efficiency and related impacts. In addition, existing treatment facilities and processes were studied with the aim of identifying possible factors affecting purification efficiency and of applying the information acquired in the design of optimisation studies conducted under laboratory conditions. Specific objectives of these optimisation studies were:

i. To examine the effectiveness of solid inorganic coagulants as purification agents in the treatment of peatland-derived runoff water and the influence of coagulant dissolution on treatment efficiency and process parameters.
ii. To evaluate the suitability of natural and synthetic organic polymers as alternative coagulants for the purification of peat extraction runoff, by comparing their performance to that achieved by the normally used metal salt coagulant.
iii. To investigate the influence of water pH, temperature and process parameters, such as mixing and settling time, on coagulant performance.
iv. To identify coagulant-specific optimum process parameters (dosage, mixing, retention time etc.) for effective purification.
v. To study the influence of coagulant type on the removal of designated pollutants such as SS, nutrients and DOC.
vi. To investigate the characteristics of DOC contained in peat extraction runoff water using fractionation analysis and determine its influence on the purification efficiency achieved by different coagulants.
vii. To evaluate the response of the chemical purification process to fluctuations in water quality that are typical of peatland-derived runoff.

In order to achieve these general and specific objectives, a research plan involving field and laboratory work was devised. The field studies included e.g. evaluation of water quality monitoring data, site observations and experiments. Field studies are referred to in this thesis as *background studies* and are described in order to support the work performed in the laboratory or optimisation phase of the research. The core of this thesis is the research conducted under laboratory conditions, which is referred to as *optimisation studies*. The results of these optimisation studies are reported in full in Papers I–IV.

During the optimisation studies, natural runoff water samples were used and experimental procedures based on jar test methodology were designed to investigate the suitability of different coagulants and the influence of process and water quality parameters on purification efficiency. Papers I–III report the results from evaluation of different types of coagulants (metal salts, synthetic polymers and natural polymers), including the influence of process and water quality parameters on overall coagulant performance. Paper IV describes the influence of variations in water quality on the coagulation-flocculation process when ferric sulphate is the coagulant added.

2 Background studies

Careful evaluation of existing treatment systems was necessary to identify factors affecting purification efficiency. During the background studies, water quality monitoring data and field observation data were used in evaluation of treatment facilities and process conditions. During site visits, water samples were collected and on-site experiments (tracer tests), measurements (discharge and added coagulant) and visual observations were performed (regarding treatment facilities and process conditions), with the objective of complementing the information provided by the monitoring data. Figure 2 shows the locations of the peat extraction sites where monitoring data were collected and the sites where water sampling was conducted during the laboratory or optimisation phase of the research.

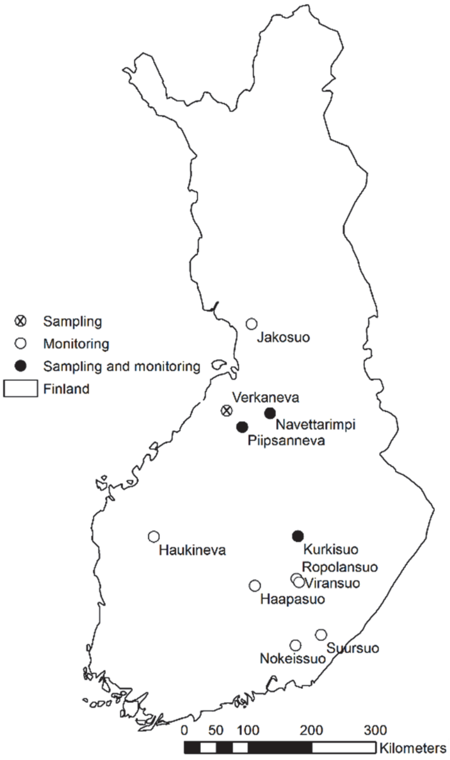


Fig. 2. Location of peat extraction sites managed by Vapo Oy for which monitoring data was available and/or at which sampling was conducted.

2.1 Methods

2.1.1 Water quality monitoring data analyses

Water quality monitoring data from for 10 peat extraction sites where at which chemical purification was is applied (taken over a 2–8 years monitoring period with either biweekly or monthly recordings between 2003 and 2011) were provided by Vapo Oy. The data sets included pollutant load (SS, COD, pH, nutrients, etc.) and purification efficiency values. Properties Components of the data sets, such as mean, variance and percentiles, were utilised in the evaluation of the quality of the collected water samples used during the optimisation studies and for thein assessment of variations in runoff water quality and purification efficiency achieved under field (or real) conditions.

2.1.2 Tracer test

The use of a conservative tracer is a quick, simple and effective way to measure discharge, retention time and flow pathways within a system (AWWA, 1996). Sodium chloride (NaCl) is a commonly used tracer due to its conservative nature and low related environmental impacts. The addition of NaCl increases the ionic strength of the water, increasing electric conductivity (EC). The magnitude of the increase in EC, which can easily be monitored by suitable sensors, is related to the amount of NaCl added to the water (AWWA, 1996).

A tracer experiment using NaCl was conducted at Navettarimpi peat extraction site, located in Vaala, Finland (Fig. 2), to identify the hydraulic conditions within the sedimentation basin. The site contains a typical small-scale treatment unit that shows fluctuations in purification efficiency. Another factor taken into consideration in selection of the site was its proximity to the University of Oulu.

Ten electric conductivity sensors were placed within the Navettarimpi sedimentation basin (Fig. 3) and connected to a central unit data logger, which enabled continuous monitoring of EC values. For determination of the required amount of tracer to be added, information on the background EC of the runoff water was required. Therefore, the sensors were installed two weeks before the tracer was added, to allow monitoring of background EC values. The amount of NaCl that needed to be added so that the concentration of tracer in the basin resulted in an increase in EC values exceeding the background EC variations (observed during the two-week monitoring period) was then determined. Calibration curves (NaCl [mg/L] plotted against EC [mS/cm]) were created for each sensor, using water samples collected from the Navettarimpi site. The mass (m) of NaCl to be added was calculated based on the estimated volume (V) of the sedimentation basin and the required tracer concentration (Equation 1):

$$m\ (g) = V\ basin(L) * Conc.NaCl\ (\frac{g}{L}) \qquad (1)$$

The pulse method of addition was utilised, where the whole tracer amount was added in one step. The NaCl (3 kg) was first diluted in a 60-L bucket and then the contents of the bucket were discharged into the dosing well (volume 1600 L). The pump (discharge Q = 160 L/s) was then activated, resulting in a 10-s pulse duration. Based on EC values measured in installed sensors, a map of the flow conditions within the basin was created. Using the data collected by the sensor installed in the basin outflow weir, the mean residence time was estimated using Equation 2 and the mass of tracer recovered was estimated using Equation 3:

$$t_{mean} = \frac{\sum_{i=1}^{i=n} ti*ci*\Delta ti}{\sum_{i=1}^{i=n} ci*\Delta ti} \qquad (2)$$

$$m_{out} = Q * \sum_{I=1}^{1=n} ci * \Delta ti \qquad (3)$$

where Q is the discharge, ci is the tracer concentration at time ti, Δti is the constant time interval (5 s) and n is the total number of data points collected.

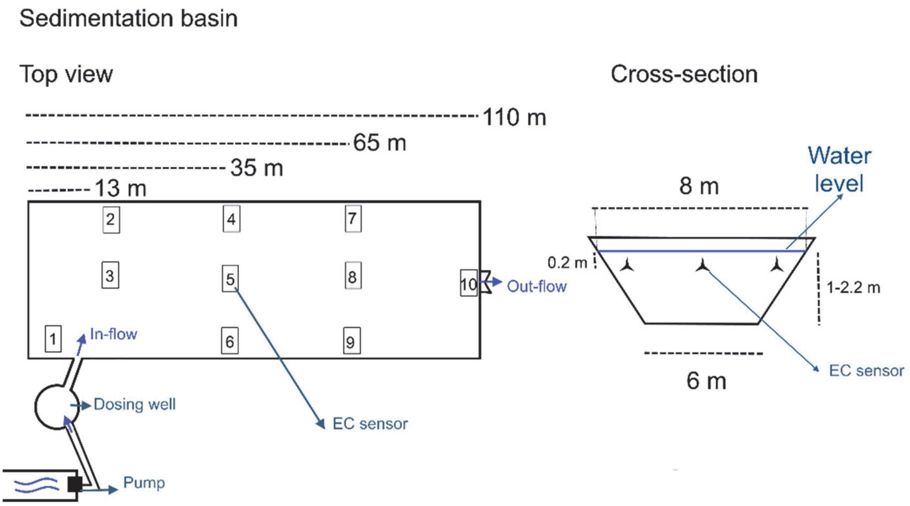


Fig. 3. Schematic diagram of the sedimentation basin at Navettarimpi site and placement of electric conductivity (EC) sensors during the tracer experiment.

2.2 Background studies: Results and discussion

Analyses of monitoring data and assessment of process conditions within existing treatment facilities emphasised the challenges of effective purification of peat extraction runoff water by chemical treatment. As mentioned in the introduction to this thesis, achieving cost-effectiveness in the use of chemical treatment is a difficult balance. While the simple structures and equipment used offer a somewhat reliable operational routine, they do not provide the level of control necessary for effective treatment. This, coupled with significant variations in water quality, can result in significant fluctuations in purification efficiency.

2.2.1 Variations in runoff water quality and purification efficiency

Analysis of water quality monitoring data revealed significant fluctuations in runoff water quality and purification results (Table 1). It is important to highlight that the values presented are a summary of data from 10 peat extraction sites where different treatment facilities, coagulant types and dosage and process parameters are used. Moreover, the data were collected between 2003 and 2011 and continuous improvement of treatment facilities has been pursued since then, so the information provided regarding purification results might not represent the current conditions. Nevertheless, the information obtained confirms that there are significant fluctuations in runoff water quality and that these should be taken into account during the design and maintenance of chemical treatment facilities. Furthermore, variations were observed in purification efficiency, highlighting the need for innovative solutions to improve the reliability of the chemical purification method.

2.2.2 Tracer test

The magnitude of the observed peaks in EC values and the difference in timing of the peaks measured by the different sensors revealed the existence of preferential flow within the Navettarimpi sedimentation basin (Fig. 4). The tracer experiment was interrupted after 4160 s (69.3 min) of tracer addition due to unpredicted lack of incoming water. At the time of test interruption, the EC values measured by sensor number 10 (discharge weir - outlet) had peaked and returned to the same magnitude as the measured background values. However, only around 70% (2.13 kg) of the added mass of tracer was recovered (Equation 3). This might be the result of back-mixing and dead zones within the basin. Nevertheless, the 70% recovery rate obtained was considered satisfactory and the test regarded as a successful tracer experiment (AWWA, 1996).

Table 1. Water quality monitoring data. Summary of information on fluctuations in runoff water quality and purification efficiency.

Parameter	Runoff water quality before treatment	Purification efficiency
SS*	0.5 mg/L < SS < 430 mg/L Mean 24 mg/L; Median 14 mg/L Higher values close to 100 mg/L were normal and only few extreme values of > 400 mg/L were recorded.	-1825% < removal < 98%, Mean 8%; Median 55%
COD**	3.5 mg/L < COD < 170 mg/L Mean 51 mg/L; Median 50 mg/L Higher values close to 70 mg/L were normal and only few extreme values of > 100 mg/L were recorded.	-150% < removal < 98%, Mean 75%; Median 81%
tot-N**	0.1 mg/L < tot-N < 7.6 mg/L Mean 2.1 mg/L; Median 2 mg/L	-74% < removal < 88%, Mean 38%; Median 39%
tot-P**	0.12 mg/L < tot-P < 0.91 mg/L Mean 0.14 mg/L; Median 0.11 mg/L	-850% < removal < 99%, Mean 83%; Median 91%
pH	2.5 < pH < 7.7 Mean 6.2; Median 6.6	2.8 < pH < 7.5 Mean 4.0; Median 3.7

*Increase in SS concentration during treatment was mostly observed for samples with low initial SS concentration and might be due to metal hydroxide precipitate formation and inadequate retention time in the sedimentation basin. In addition, a few extreme values might be connected to maintenance work on the sedimentation unit at specific sites.

** Increases in COD, tot-N and tot-P concentration during treatment might be due to lateral discharge of runoff water into the sedimentation basin during wet conditions. In addition, a few extreme values might be connected to maintenance work on the sedimentation unit at specific sites.

The calculated (Equation 2) mean retention time of the tracer in the basin was 50 min (3000 s), which is significantly lower than the estimated hydraulic retention time (basin volume/discharge) of over 200 min. The occurrence of preferential flow within a sedimentation basin can result in severe detrimental effects on purification efficiency. Flocs formed by the reaction of the coagulant do not have the required time to grow and settle and are washed out of the basin with the discharging water. According to long-term water quality monitoring data for the study site, significant fluctuations and low overall removal of SS occurred and can be attributed, at least partly, to the hydraulic conditions identified within the basin.

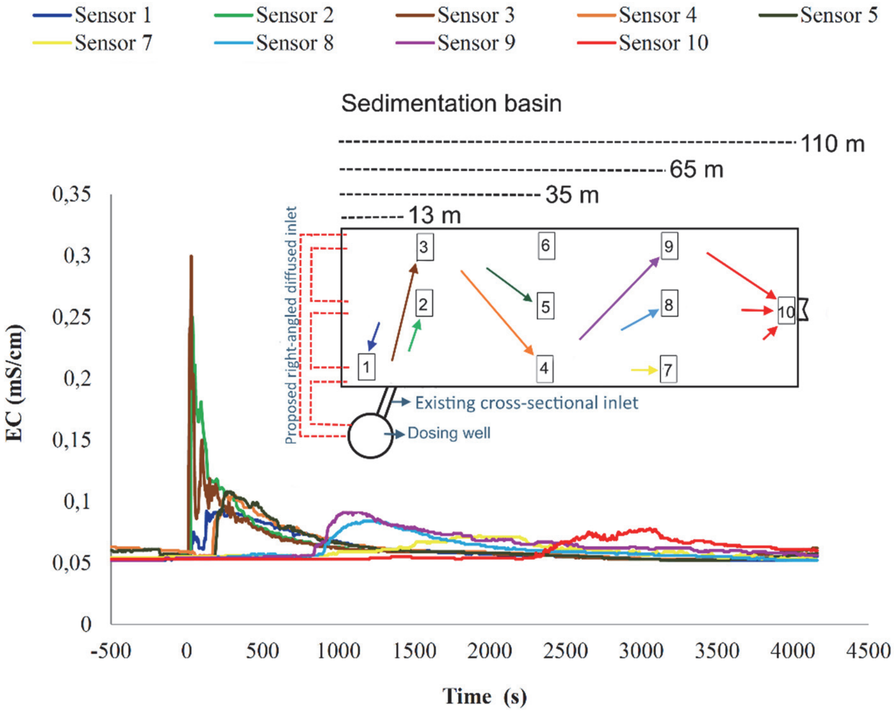


Fig. 4. Variations in electric conductivity with time due to tracer concentration plus the schematic of preferential flow observed within the sedimentation basin (note: 0 seconds = time of trace addition and sensor 6 malfunctioned).

The existence of preferential flow appeared to be the result of the cross-sectional inlet characteristics of the treatment unit (Fig. 4) and the high discharge produced by the pump (100 L/s). Based on the results, additional studies were carried out (not included in this thesis) to investigate the influence of inlet structures in the flow patterns within the basin (Mohammadighavam *et al.*, 2015a). A three-dimensional (3D) computational fluid dynamic (CFD) model was used to investigate the influence of different inlet designs on hydraulic conditions. Those studies found that inlet structures had a significant influence on retention time and flow patterns. They also found that simple and low cost inlet modifications (such as right-angled diffused inlet) could increase residence time significantly and consequently reduce the detrimental effects of preferential flow (Mohammadighavam *et al.*, 2015a).

Another issue was detected during site visits through visual observations and the tracer experiment, namely lack of appropriate slow mixing for an effective flocculation process. As previously described, in normal treatment facilities, high turbulence for the spread of coagulant is provided by the pumping system. The runoff water is transferred from the ditch network into the dosing well, which discharges into the sedimentation basin (Fig. 3). Although the flow of water throughout the basin provides some fluid motion and therefore the opportunity for flocculation to occur, the lack of adequate mixing for effective flocculation presumably had a significant effect on the purification levels observed. The influence of mixing on coagulation/flocculation with solid metal salts as the coagulant was thus evaluated under laboratory conditions during the optimisation studies (section 4.4).

3 Materials and methods

In the development and optimisation of coagulation-flocculation processes, some of the most important steps are to identify: (i) the most suitable coagulant(s) for the type of water in question, (ii) the required dosage of coagulant(s) and (iii) the influence of process conditions (water pH and temperature, mixing etc.) on coagulant performance (Bratby, 2006). These steps were followed in the optimisation studies in this thesis, the results of which are reported in Papers IIV. The methods applied during these optimisation studies are briefly summarised here and are described in detail in the original publications (I–V). All tests were performed under laboratory conditions and the research was conducted in sequential phases, each resulting in an article.

Phase 1 (Paper I): The suitability of different solid metal salt coagulants for the purification of peat extraction runoff water was studied by evaluation of dosage requirements and purification efficiency (removal of target substances and settling characteristics of flocs formed). Furthermore, the influence of process and water quality parameters (pH, temperature and mixing) on coagulant performance was investigated, as was the effect of pre-dissolution of the solid products on treatment efficiency and process requirements such as mixing and settling time.

Phase 2 (Paper II): The ability of synthetic organic polymers to act as primary coagulants in the purification of peat extraction runoff was evaluated. The best performing metal salt coagulant from phase 1 was selected and its performance (removal efficiency and settling characteristics) compared to that of selected synthetic organic polymers. The influence of water pH and temperature on purification results was also investigated.

Phase 3 (Paper III): The efficiency of the best performing metal salt (phase 1) and synthetic organic polymer (phase 2) tested was compared to that of natural organic polymers. Particular attention was paid to removal of organic matter by the test coagulants. Organic matter fractionation analysis (size-exclusion liquid chromatography coupled with organic carbon and organic nitrogen detection, LC-OCD-OND) was performed on the raw water and treated samples, in order to evaluate the effect of coagulant type on the removal of different dissolved organic fractions. The influence of water pH on coagulant performance was also studied.

Phase 4 (Paper IV): Ferric sulphate was selected as the coagulant agent for this phase of the tests, since it is the metal salt normally used at peat extraction sites. The influence of variations in water quality (typical in peat extraction runoff) on purification efficiency was investigated. A factorial design was used in the experimental procedure and the results were evaluated using statistical methods (Analysis of Variance (ANOVA) and orthogonal contrast (OC) calculations).

3.1 Peat extraction runoff water quality

Throughout the optimisation studies, samples were collected in 35-L containers from different peat extraction sites in Finland (Fig. 2) and stored at 5–10 °C for the duration of the test period (I–IV). A series of water quality analyses were conducted on each sample at in-house facilities and by outsourced laboratories. General characteristics of the runoff water samples are presented in Table 2, where samples 1 (Navettarimpi) and 2 (Piipsaneva) are from Paper I, sample 3 (Kurkisuo) is from Paper II, samples 4 and 5 (Verkanneva) are from Paper III and samples 6 (Navettarimpi) and 7 (Verkanneva) are from Paper IV.

For evaluation of the influence of variations in water quality on purification efficiency (Paper IV), samples 6 and 7 were combined and manipulated to produce eight sub-samples for testing. The procedures used during the sample manipulation process and the characteristics of the subsamples created are described in section 3.5. In general, water quality analyses (Table 2) were performed in each 35-L container 'as is', in order to ensure accurate initial conditions and to evaluate possible changes in water quality during the storage period. Constant monitoring of pH, turbidity, colour and temperature of the samples was conducted before each jar test experiment. Water quality analyses (raw water and treated samples) conducted at the in-house laboratory and standard methods used are presented in Table 3.

Charge quantity (Cq) measurements were performed using the Mütek particle charge detector PCD 03 PH following the equipment manual. The method measures the total surface charge contained in the suspension using the streaming current principle. The samples were titrated using either cationic or anionic polyelectrolyte (0.001 eq/L) until the charge of the sample was neutralised. The Cq value (eq/L) of the sample was then determined based on the concentration and amount of polymer required for neutralisation of fixed-volume samples. Zeta (ζ) potential measurements were performed using a Delsa Nano C Particle Analyser (detection range 0.6 nm-7 mm). The performance of the equipment was checked using a mobility control (Otsuka Electronics Co, Ltd.) containing polystyrene latex particles. Specific UV absorbance (SUVA) was determined as (Papers III and IV): SUVA = UV254 abs./DOC (L/mg-m).

Water quality analyses (raw water and treated samples) were performed by the certified Finnish Environment Institute laboratory, Oulu, Finland (for SFS-EN and ISO standard methods used, please refer to Papers I–IV). These included: Total phosphorus (tot-P) (Papers I–IV), phosphate-phosphorus (PO4-P) (Papers I–IV), total iron (Fe) (Papers I–IV), sulphate (SO_4^{2-}) (Papers III and IV), total nitrogen (tot-N) (Papers I–IV), alkalinity (Alk) (Paper III), total organic carbon (TOC) (Papers I and II), DOC (Paper IV); pH (I) and SS (Papers I, II and IV).

Organic matter fractionation analyses (Papers III) were performed by DOC-Labor (Eisenbahnstrasse, Germany) using the LC-OCD-OND technique as fully described in Huber et al. (2011). The method separates DOC into hydrophobic organic carbon (HOC) and chromatographic dissolved organic carbon (CDOC). HOC is determined as the difference between DOC and CDOC and thus all organic carbon retained in the chromatography column is, in this context, defined as ‘hydrophobic’. The CDOC fraction (described as having a hydrophilic nature) is further segregated into the following fractions: biopolymers (polysaccharides, proteins and amino sugars, MW>10000 g/mol); humic substances (HS; MW 500–1000 g/mol); building blocks (breakdown products of HS; MW 300–500 g/mol); low MW (LMW) neutrals such as alcohols, aldehydes, ketones, sugars (MW<350 g/mol); and LMW acids (MW<350 g/mol) (Huber et al., 2011). Jar test experiments were performed in which the optimum dosage of selected coagulants was applied. Raw water (samples 4 and 5) and treated samples (two replicates) were stored in 50-mL plastic bottles and individually packed following the instructions of the receiving laboratory (DOC-Labor). Samples were dispatched, received and analysed within 72 hours.

Table 2. Water quality characteristics of samples tested.

Water quality parameters	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
	Navettarimpi	Piipsaneva	Kurkisuo	Verkanneva	Verkanneva	Navettarimpi	Verkanneva
TOC (mg/L)	27.0	27.5	30.7				
DOC (mg/L)				76.2	80.8	18	72
Colour (mg Pt/L)	320	300	396	750	728		
SS (mg/L)	17.1	18.8	20.8	7.5	5.9	240	11
Turbidity (NTU)	17.0	25.5	50.5	6.9	6.4		
tot-P (µg/L)	58.0	61.0	74.7	107.0	115.0	280	190
PO_4-P (µg/L)	24.0	21.0	44.2	34.5	33.0	150	57
tot-N (mg/L)	1.72	2.00	2.20	2.30	2.20		
Fe (mg/L)	3.83	2.15	6.70	4.40	4.45		
$SO4^{2-}$ (mg/L)				4.9	4.5		
Cq (µeq/L)				-242	-390		
ζ-potential (mV)				-19.4	-23.1		
SUVA (L/mg-m)			3.0	3.8	3.9		
Alk (mmol/L)				0.03	0.38		
pH	6.5–6.8	5.5–5.9	6.5	4.5	6.6	6.5	4.5

Table 3. Water quality analysis performed at the in-house laboratory. Methods and equipment used.

Water quality parameter	Method	Equipment
Suspended solids (SS) (III and IV) (mg/L)	(1.2 µm filtration) SFS-EN 872:2005	Vacuum suction Class fibre filter Whatman GF/C
Turbidity (I–IV) (NTU)	EN 27027:1994	Hatch Ratio/XR Turbidity meter
Colour (I–IV) (mgPt/L)	ISO 7887:1994	Lovibond Nessleriser Daylight 2000
pH (I–IV)	SFS-EN 13037:1994	WTW Universal meter
Charge quantity (Cq) (III and IV) (eq/L)	Equipment manual (described in text)	Mütek particle charge detector PCD 03 PH (Mütek Analytic GmbH, Germany)
Zeta (ζ) potential (mV)	Equipment manual (described in text)	Delsa Nano C Particle Analyser (detection size range 0.6 nm–7 mm)
Ultraviolet absorbance at 254 nm (UV254 abs.) (III and VI) (cm-1)	Equipment manual (0.45 µm filtration)	UV 1800 spectrophotometer equipment (Shimadzu, Japan)
Dissolved organic carbon (DOC) (mg/L)	Equipment manual (0.45 µm filtration).	Sievers 900 portable total organic carbon (TOC) analyser

3.2 Characteristics of coagulants tested

All coagulants tested were commercially available products (Table 4). In the first phase (Paper I) of tests, three solid (sol) metal salts were studied: Aluminium sulphate (Alum sol); ferric sulphate (FS sol); and ferric aluminium sulphate (mixture of 15% ferric sulphate and 85% aluminium sulphate), referred to as Alum+FS sol. Purification conditions were also evaluated for pre-dissolved (pd) stock solutions (10 g/L) of aluminium sulphate (Alum pd) and ferric sulphate (FS pd) to evaluate the effects of coagulant dissolution on treatment performance. In the second phase (Paper II), all coagulants tested were supplied in liquid (solution) form. The efficiency of two synthetic organic polymers, poly(diallyldimethyl) ammonium chloride (pDMAC) and epichlorohydrin-dimethylamine copolymer (pAmine), was compared to that achieved by FS (liquid). In the third phase (Paper III) of tests, synthetic and natural organic polymers were evaluated against FS (liquid). The organic polymers were: pDMAC (liquid), two tannin-based products (Tan1 and Tan2, liquid) and chitosan (Chit, solid). Solid FS was the coagulant of choice in the fourth and final testing phase (Paper IV), in which the coagulant was pre-dissolved prior to addition, i.e. the coagulant was dosed as a stock solution.

When applicable, stock solutions were prepared by dilution of the commercially supplied products with deionised water. The only exception was chitosan, the stock solution of which was prepared by dissolving the solid product (2.5 g) in a solution containing acetic acid 100% (5 mL) and deionised water (492.5 mL). Reported dosages refer to the ‘effective dosage’ of the coagulant, calculated from the volume or mass dosed and the percentage of dry solids (active ingredient) contained in the products supplied (Table 4).

Data on the MW of pDMAC and Chit (Table 4) were provided by the suppliers. The average MW of the tannin-based polymers was determined by an out-sourced laboratory at Åbo Academy University, Turku, Finland. A full description of the methodology used is provided in Song et al. (2008). Data on the CD (Table 4) of pDMAC and pAmine was supplied by the manufacturer, while the CD of the natural polymers was determined at the in-house laboratory using the Mütek particle charge detector PCD 03 PH. Polymer solutions of varying concentrations were prepared and Cq measurements were performed following the methodology previously described. The CD of the polymers (eq/g) was calculated based on the concentration of the coagulant solutions.

3.3 Jar test procedures

Coagulation-flocculation studies were performed using the jar test methodology. A six (1-L) jar programmable paddle stirrer of model Flocculator 2000 (Kemira Kemwater) was used (Fig. 5). During the evaluation of dosage requirements, increasing doses of coagulant were added sequentially to 1-L samples (2–3 replicates). Mixing parameters applied were: (Paper I) pd/sol coagulants: 300/400 rpm for 10/60 s, 50/70 rpm for 25/15 min followed by 30 minutes of sedimentation; (Papers II–IV) 300 rpm for 10 s followed by 50 rpm for 25 min and 30 min of sedimentation. Supernatant water samples were collected (200–400 mL) and purification efficiency was first evaluated by measurements of colour (Papers I-IV), turbidity (Papers I–IV), pH (Papers I–IV), temperature (Papers I–IV), Cq (Paper III) and ζ-potential (Paper III). Dosage requirement curves were then constructed, as shown in Figure 6 using the example of dosage curves from phase 3 of tests (Paper III). The dose which provided the best removal of colour and turbidity, with low variation among experimental replicates, was identified as the optimum dosage rate of the coagulants.

Table 4. Characteristics of coagulants tested.

Metal salt coagulants	Density	Dry solids	Active substance	Supplier	Paper
FS [Fe2(SO4)3.nH2O] (liquid)	1550 kg/m3	42%	2.1 mol/kg	Kemira Oyj, Kemwater, Finland	(II)
FS [Fe2(SO4)3.nH2O] (solid)	1200 kg/m3	100%	3.5 mol/kg	Kemira Oyj, Kemwater, Finland	(I and IV)
Alum [Al2(SO4)3.nH2O] (solid)	910 kg/m3	100%	3.5 mol/kg	Kemira Oyj, Kemwater, Finland	(I)
Alum (85%) + FS (15%) (solid)	1000 kg/m3	100%	3.5 mol/kg	Kemira Oyj, Kemwater, Finland	(I)
Organic coagulants	Molecular weight	Dry solids	Charge density	Supplier	Paper
pDMAC	200000 g/mol	20%	6 meq/g	Kemira Oyj, Kemwater, Finland	(II and III)
Synthetic - liquid	Supplied		Supplied		
pAmine	10000 g/mol	50%	7 meq/g	Kemira Oyj, Kemwater, Finland	(II)
Synthetic - liquid	Supplied		Supplied		
Tan1	300 g/mol	25%	2.3 meq/g	Grove Advanced Chemicals, Portugal	(III)
Natural - liquid	Measured		Measured		
Tan2	1800 g/mol	25%	2.2 meq/g	Grove Advanced Chemicals, Portugal	(III)
Natural - liquid	Measured		Measured		
Chit	350000 g/mol	100%	5.2 meq/g	Sigma Aldrich, USA	(III)
Natural - solid	Supplied		Measured		

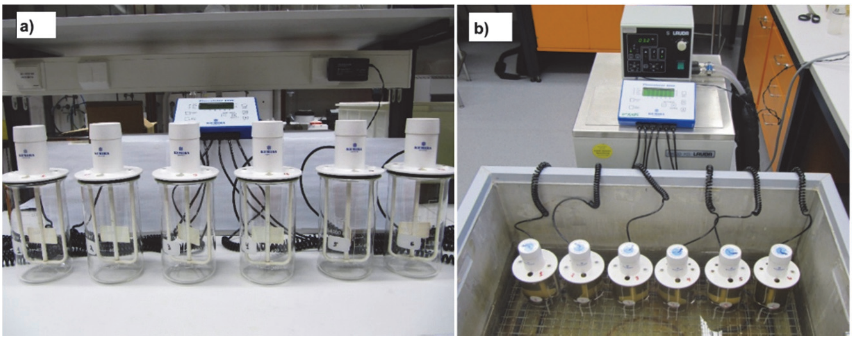


Fig. 5. Jar test equipment in (a) the normal experimental set-up and (b) inside a temperature-controlled insulated water tank (Heiderscheidt, 2011).

For the evaluation of overall purification efficiency, samples purified with the optimum dosage of individual coagulants (2–3 replicates) were analysed for a series of water quality parameters such as TOC, DOC, tot-P, PO4-P, tot-N, Fe, SS, Alk etc.

The settling characteristics of flocs formed were investigated using 1-L jars (height = 19 cm and diameter = 9 cm) according to the method outlined in Bratby (2006). Runoff water samples were treated with the optimum dosage of coagulants. During the sedimentation process, 30-mL samples were collected at constant jar depth (8 cm from the bottom) at pre-determined time intervals (1, 2, 3, 4, 6, 8, 11, 13, 17, 25 min.). Turbidity measurements were then performed on these samples (2 replicates).

The influence of temperature (Paper I = 5 °C, Paper II = 2°C) on the purification process was investigated by transferring the jar test equipment to a temperature-controlled insulated water tank (Fig. 5b). The procedures described above for evaluation of purification efficiency and settling characteristics were then performed (2 replicates).

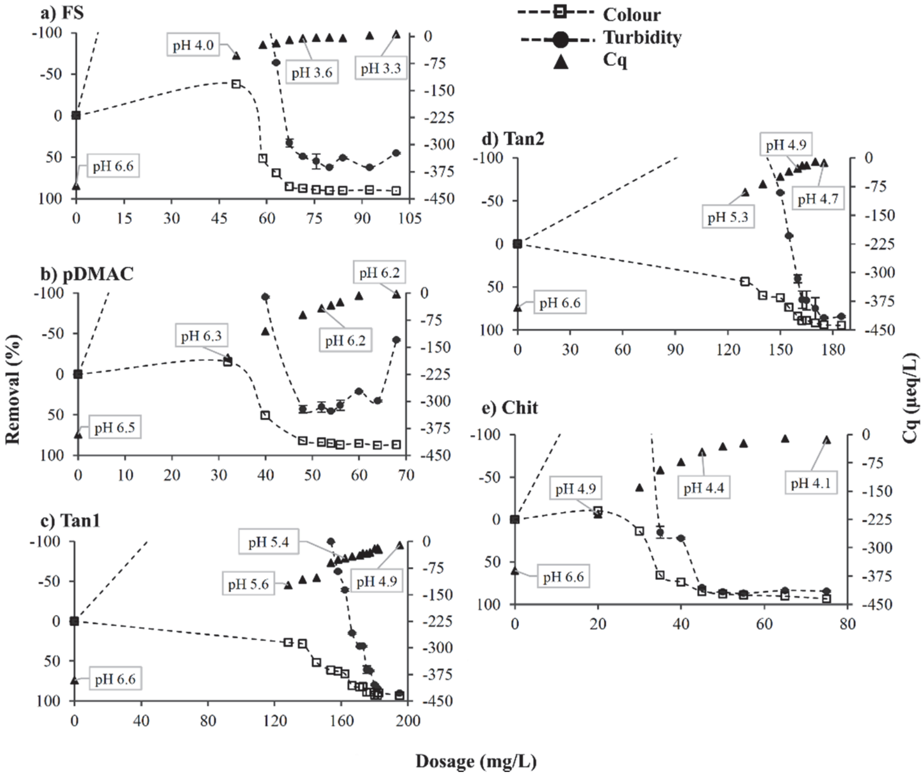


Fig. 6. Example of dosage requirement curves constructed during evaluation of coagulant dosages needed for effective purification. Removal of colour and turbidity with increasing dosages of coagulants as well as purified water pH and charge quantity (Cq) (Paper III; revised and reprinted with permission from Elsevier).

3.4 Optimisation of mixing parameters

Mixing is an important parameter in coagulation-flocculation processes. Mixing is required for blending the coagulant at the point of addition and for enabling particle collision and aggregation after the initial chemical destabilisation. Introducing shear motion in a liquid creates velocity gradients within the liquid mass. Camp and Stain (1943) developed the root mean square velocity gradient (G) principle and proposed that G could be used as a design parameter for coagulation-flocculation facilities. G (s^{-1}) is expressed as a function of the total energy input per total tank volume (Equations 4 and 5).

$$G = \sqrt{\frac{W}{\mu}} \tag{4}$$

$$W = \frac{P}{V} \tag{5}$$

where W is the power dissipation function, P (Nm/s) is the power drawn by the mixing device, V (m^3) is the volume of the tank (vessel, container etc.) and μ (Ns/m^2) is the absolute viscosity of water.

The one factor-at-a-time method was used in the design of experiments to investigate the influence of mixing parameters on purification results of solid and pre-dissolved metal salt coagulants (paper I). Optimum coagulants dosages were applied and the jar-test procedure utilized. Four mixing parameters were evaluated: slow mixing time (5, 10, 15 and 25 min), slow mixing speed (20, 50, 70 and 90 rpm), fast mixing time (10, 60 and 120 s) and fast mixing speed (100, 200, 300 and 400 rpm). The tests were performed in sequential stages where in each stage three parameters were kept constant while the fourth parameter was systematically varied. Two replicate runs of each test were executed in which turbidity and colour measurements were performed. Samples from the replicate runs with the highest and lowest removal of turbidity were then further analysed for SS, tot-P, PO4-P, tot-N and TOC.

The root mean square velocity gradient (G s^{-1}) induced in the fluid mass was determined using Equations 4 and 5. In the jar test equipment used (Fig. 5), mixing was provided by a mechanical mixer with rotating blades. The power (P) drawn by a mechanical mixer with rotating blades is given by Equation 6.

$$P = \phi * \rho * n^3 * D^5 \tag{6}$$

where ϕ (3.5) is a dimensionless power number related to mixing device and container geometry (extracted from Bratby, 2006), n is the mixer rotational speed in revolutions per second, ρ (kg/m^3) is water density; and D is the diameter (m) of the mixer impeller.

3.5 Influence of water quality variations on purification efficiency - Factorial design

For evaluation of the influence of water quality variations on purification efficiency (Paper IV), a 24 factorial design was applied in the jar test experiment. The study investigated how the variation in four selected factors between two levels (high and low) affected purification efficiency, represented by the residual concentration of pollutant substances (response variables).

Selection of factors and response variables

The factors evaluated were: organic matter concentration as DOC (factor A); SS concentration (factor B); initial water pH (factor C); and coagulant (FS pd) dosage used (factor D). Statistical analysis of water quality monitoring data (as described in section 2.1.1) was used to identify the range of factor variations to be applied. The 10th and 90th percentile of observed values for DOC, SS and pH were selected as the low and high concentration (or levels), respectively, of each factor (Table 5). High and low levels of the fourth factor, coagulant dosage (Dos), were selected via dosage requirement identification tests (for further details, see Paper IV). The influence of the four factors on purification efficiency was assessed by evaluation of observed changes in the residual concentrations of the three selected response variables (DOC, SS and tot-P).

Table 5. Selected high and low levels for the factors evaluated in the 2^4 factorial design (Paper IV; reprinted with permission from Elsevier).

Water quality parameters	Factors	Level	
		Low	High
DOC (mg/L)	A	20	70
SS (mg/L)	B	10	60
pH	C	4.5	7.0
Coagulant FS pd (mg/L)	D	35	100

Preparation of water samples and statistical analyses

The purification tests required eight water samples containing the low and high concentration combinations of DOC, SS and pH (Table 5). Two natural samples were used (samples 6 and 7, Table 2) in preparation of these eight samples. The samples preparation process is described in Figure 7. To prepare samples with high SS, sample 6, which contained high SS concentration, was centrifuged (4000 rpm, 4 min) and the sediment added to sample 7, while the supernatant was discarded. Samples with low concentrations of all factors were prepared by diluting sample 7 (plus added sediments) with deionised water. Samples with high pH (7.0) values were prepared by addition of sodium hydroxide (NaOH, 0.1 M).

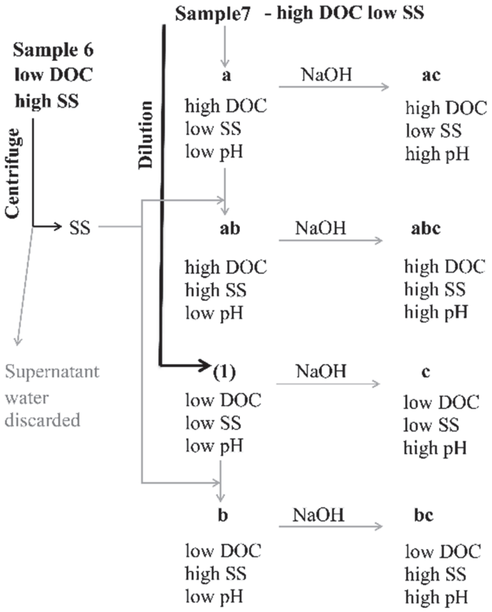


Fig. 7. Diagram describing the sample preparation process (Paper IV; reprinted with permission from Elsevier).

The eight samples created (Table 6) were then treated with low and high coagulant dosages, resulting in 16 experimental runs (3 replicates). The prepared samples and the experimental runs (referred to as treatment combinations) are hereafter denoted by lower case letters (a–d) representing factors A–D in the case of high levels, while low levels of a factor are denoted by the absence of the corresponding letter. Thus a sample or treatment combination identified by the letter ‘a’ refers to a sample where DOC concentration (factor A) was kept at a high level while all other factors were at their low levels. The sample containing low concentrations of all controlled factors is denoted (1). The outputs of the three replicates of the 16 experimental runs were analysed using SPSS statistical software. The magnitude and the direction of factor effect were determined by orthogonal contrast (OC) calculations (Equations 7 and 8) and the significance of the factor effects was evaluated using ANOVA.

The treatment combinations corresponding to the 16 experimental runs performed are presented in standard order or Yate’s order (Yates, 1937): (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, abcd. The effect of a factor is defined as the change in the response variable caused by a change in the level of that factor, averaged over the levels of the other factors. When the factor effect depends on the applied level of one or more other factors, an interaction effect is said to occur (Montgomery, 2006). The algebraic signs applied in the determination of OC (Equation 7) followed the method outlined in Montgomery (2006). The effects of individual factors or the effect of interaction between factors are by convention indicated with the capital Latin letter corresponding to those factors, e.g. the effect of factor A (DOC) is represented by the letter A. The interaction effect between factor A (DOC) and factor B (SS) is denoted AB and so forth.

$$OC_{A\,B\ldots K} = (a\ \pm 1)(b \pm 1)\ldots(k\ \pm 1) \quad (7)$$

$$A, B, \ldots K = \frac{2}{n2^k}\,(OC_{A\,B\ldots K})^2 \quad (8)$$

where $OC_{A\,B\ldots\,K}$ is orthogonal contrast of factors, A, B…, K; a, b …, k is the total of all replicates for the treatment combination; A B… K is the magnitude of the factor effect and n is number of replicates.

Table 6. Water quality characteristics of the eight samples prepared (Paper IV; reprinted with permission from Elsevier).

Samples	Controlled factors			Other measured substances			
	A DOC (mg/L)	B SS (mg/L)	C pH	tot-P (µg/L)	PO_4-P (µg/L)	UV_{254} abs. (1/cm)	Cq (µeq/L)
(1)	19.6	7.7	4.6	23	6	0.708	-89
a	73.0	8.6	4.5	75	23	2.520	-246
b	17.9	59.5	4.7	63	34	0.690	-63
ab	66.0	60.0	4.5	100	44	2.340	-222
c	20.5	8.4	6.9	24	5	0.734	-111
ac	71.7	10.0	6.6	72	21	2.550	-406
bc	17.6	65.3	6.5	65	33	0.700	-95
abc	66.6	58.5	6.9	110	43	2.390	-359

4 Results and discussion

In order to evaluate and optimise the chemical treatment method applied in the purification of peat extraction runoff, a strategy was created and the following steps followed: (i) evaluation and identification of the most suitable coagulants in terms of dosage and purification efficiency; (ii) evaluation of the influence of process and water quality parameters (mixing, water pH and temperature) on coagulant performance; (iii) evaluation of the influence of variation in water quality on purification efficiency; and iv) development of guidelines aimed at decreasing fluctuations in purification efficiency, increasing the reliability and reproducibility of the method and thus reducing its impacts.

4.1 Coagulant evaluation

4.1.1 Solid metal salts and the effect of pre-dissolution (I)

The efficiency of selected solid metal salt coagulants (Alum sol, FS sol and Alum+FS sol) was investigated. Purification conditions were also evaluated for pre-dissolved coagulants (Alum pd and FS pd) with the objective of evaluating the effects of coagulant dissolution on treatment performance. The dose which provided the best removal of colour and turbidity, with low variation among experimental replicates, was identified as the optimum dosage of the coagulants (Table 7).

Table 7. Optimum dosage range and selected optimum dosage in the purification of samples 1 and 2 (Paper I, revised and reprinted with permission from Elsevier).

Water sample	Coagulant	Optimum dosage range (mg/L)	Selected optimum dosage (mg/L)
1	Alum sol	60 – 80	70
1	Alum pd	60 – 80	70
1	FS sol	60 – 80	70
1	FS pd	50 – 70	60
1	Alum+FS sol	70 – 90	70
2	Alum sol	80 – 140	140
2	Alum pd	70 – 90	80
2	FS sol	50 – 70	70
2	FS pd	50 – 70	50
2	Alum+FS sol	80 – 90	90

In general, the optimum dosages identified for pre-dissolved coagulants were up to 30% lower than those identified for solid coagulants. Re-evaluation of the dosage requirements obtained during the work in this thesis revealed that the optimum dosage of Alum sol identified in the purification of sample 2 was initially overestimated (Table 7). Although results from replicates where lower dosages were applied displayed significant variations in colour and turbidity removal rates, if the same evaluation methodology as in subsequent studies (II–IV) had been applied, the selected optimum dosage would have ranged between 80 and 100 mg/L. Nevertheless, based on the results obtained for the treatment of sample 1, it can be concluded with confidence that the overestimation of the dosage of Alum sol in the treatment of sample 2 did not affect the main findings reported in Paper I.

When the identified optimum dosages were applied, all coagulants achieved high load reduction levels, with pre-dissolved coagulants being the most efficient and displaying lower variation between replicates (Fig. 8). In particular, the removal of SS was significantly higher (<30%) for pre-dissolved coagulants. This indicates that pre-dissolution of the solid coagulants had a significant influence on the flocculation stage and outcome of the purification process. Among the metal salts tested, ferric sulphate was the best performing in both pre-dissolved and solid form, e.g. the removal of TOC was substantially higher (20–35%) when FS was applied.

Removal efficiencies achieved in the purification of sample 1 (Fig. 8a) were generally higher than those achieved in the purification of sample 2 (Fig. 8b), especially for aluminium-based coagulants. The water quality characteristics of samples 1 and 2 were similar (Table 2), but sample 2 showed slightly lower pH (see section 4.2 for the influence of pH on purification) and higher turbidity (see section 4.6 for the influence of SS concentration on purification). The addition of all coagulants had a significant impact on water pH, indicating that samples 1 and 2 contained low alkalinity and thus low buffering capacity.

The settling characteristics of the flocs formed is an important factor in the evaluation of coagulants performance. It represents the ability of the coagulant to provide flocs that can readily sediment, resulting in clarified supernatant water.

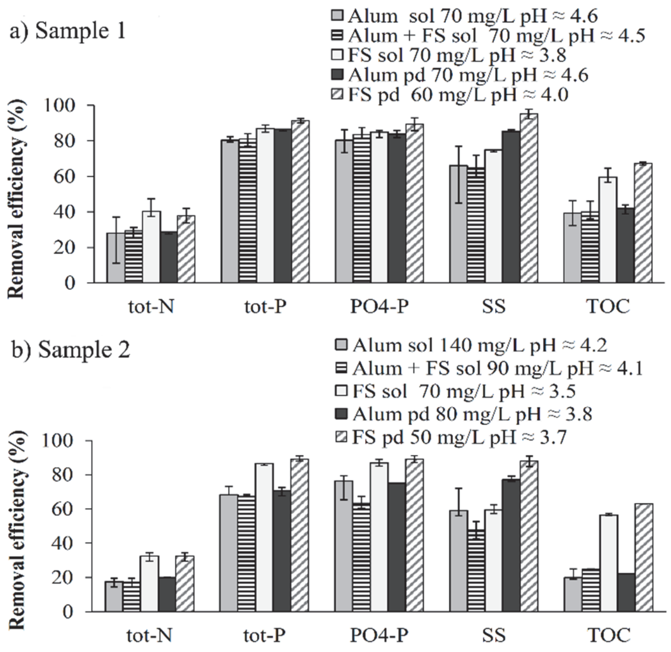


Fig. 8. Average removal efficiency (maximum and minimum values of 3 experiment replicates represented by error bars) achieved by the optimum dosages of solid (sol) and pre-dissolved (pd) coagulants and the resulting pH in the purification of sample 1 and sample 2 at 20 °C (Paper I; revised and reprinted with permission from Elsevier).

Addition of the metal salt coagulants to both water samples resulted in an increase in initial turbidity (sample 1 = 17 NTU, sample 2 = 25 NTU), although this increase was more accentuated in the purification of sample 2 (Fig. 9). The reported turbidity values for time ‘0 minutes’ (Fig. 9) represents the turbidity measured at the end of the flocculation process (end of mixing, pre-sedimentation). During the coagulation process, the formation of insoluble complexes and hydrolysis products increases the number of particles in suspension (Duan and Gregory 2003). This, coupled with the increase in particle (floc) size during the flocculation process, can explain the increase in turbidity observed.

Among the coagulants tested, FS produced the fastest sedimentation rates and overall higher clarification of the supernatant water. When applied in solid form, FS achieved 80% removal of pre-sedimentation turbidity within 4 min of settling in the purification of both water samples, while Alum sol and Alum+FS sol required between 11 and 25 minutes (Fig. 9). The settling characteristics of the pre-dissolved salts mostly reflected the patterns observed for the solid coagulants. However, some differences were apparent at the beginning of sedimentation, when the solid coagulants appeared to display somewhat faster settling rates, and at the end of sedimentation, when the pre-dissolved coagulants displayed slightly better supernatant water clarification (Fig. 9). It appears that, the addition of solid coagulants resulted in the formation or smaller flocs which stayed in suspension, leading to lower clarification of the water and consequently to lower SS removal (Fig. 8).

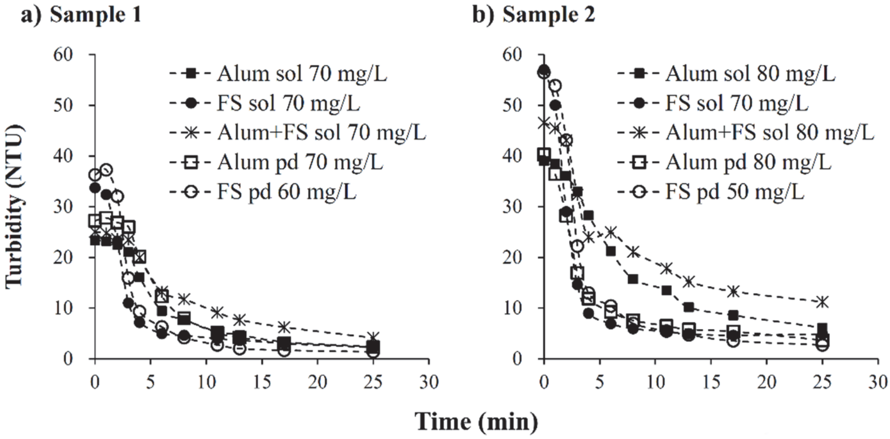


Fig. 9. Settling characteristics (removal of turbidity with time) of flocs formed by the optimum dosages of solid (sol) and pre-dissolved (pd) coagulants at 20 °C.

Based on the results obtained, ferric sulphate was identified as the best inorganic coagulant among the metal salts tested for the purification of peat extraction runoff water. The pre-dissolution of coagulants proved to be beneficial for coagulant performance, improving treatment conditions. The suitability of alternative (organic) coagulants was subsequently tested against the performance of FS.

4.1.2 Synthetic organic polymers compared to ferric sulphate (II)

In the second phase of tests (Paper II), the performance of selected synthetic organic polymers (pDMAC and pAmine) as coagulant agents in the purification of peat extraction runoff water (sample 3) was compared to that of FS (liquid) (Fig. 10). In terms of dosage requirements, FS required significantly higher dosages than the synthetic organic polymers for satisfactory removal of colour and turbidity. The optimum coagulant dosage identified was: FS 84 mg/L, pDMAC 16 mg/L and pAmine 25 mg/L. The pH of samples treated with the synthetic organic polymers remained mostly constant around the natural pH of the raw water (6.5), whereas the pH of samples treated with FS decreased substantially, to values close to 4 (Fig. 10).

At the optimum dosage, FS achieved higher overall purification efficiency than the synthetic organic coagulants, with the removal of TOC being especially high (~77%) when FS was applied (Fig. 10). In general, high removal of tot-P (>88%), PO4-P (>90%) and SS (>85%) was achieved by all coagulants. An increase in tot-N residual concentration was consistently found in samples treated with pAmine. Among the synthetic polymers, pDMAC displayed better coagulation performance than pAmine, as it required lower dosage and achieved higher removal of tot-N, SS and TOC.

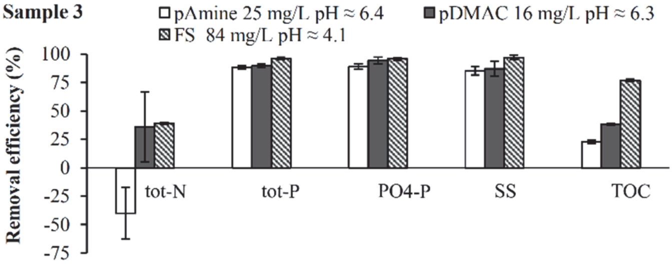


Fig. 10. Average removal efficiency (maximum and minimum values of three experimental replicates represented by error bars) achieved by the optimum dosage of coagulants at 20 °C in the purification of sample 3 (Paper II; revised and reprinted with permission from Taylor & Francis).

When evaluating the settling characteristics of flocs formed by the addition of the optimum dosage of the coagulants, FS displayed the fastest sedimentation rates in the initial and most important stages of the sedimentation process (Fig. 11). FS achieved 80% removal of pre-sedimentation turbidity after about 10 min of settling, while both of the synthetic organic polymers reached the 80% removal mark at around 13 min. FS also achieved the best clarification of the supernatant water in the final stages of sedimentation. This occurred despite the pre-sedimentation (end of flocculation) turbidity observed in FS-treated samples being significantly higher than that observed in polymer-treated samples (Fig. 11).

In general, FS was the best performing coagulant. Among the organic polymers, pDMAC required a lower dosage and showed better purification efficiency than pAmine, and was therefore selected to move forward to the next phase of tests.

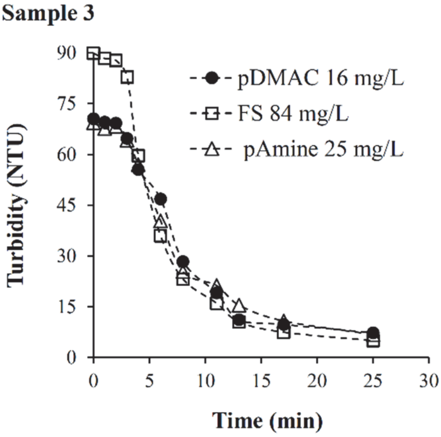


Fig. 11. Settling characteristics (removal of turbidity with time) of flocs formed by the optimum dosage of coagulants in the purification of sample 3 at 20 °C.

4.1.3 Natural organic polymers compared to ferric sulphate and pDMAC (III)

The performance of natural organic polymers (Chit, Tan1 and Tan2) was compared to that of FS and pDMAC in the purification of sample 4. In general, Chit and pDMAC required a significantly lower dosage (40–55%) than FS, while the tannin-based coagulants required a substantially higher dosage (55–75%). The optimum coagulant dosage identified was: FS 71 mg/L, pDMAC 32 mg/L, Tan1 120 mg/L, Tan2 110 mg/L and Chit 40 mg/L. During dosage requirement tests, among the tannin-based products Tan2 showed higher removal of colour and turbidity at lower dosages than Tan1 (Fig. 6). Therefore, Tan2 was the tannin-based product selected for evaluation of overall purification efficiency, where it was compared to FS, pDMAC and Chit (Fig. 12).

Due to the low alkalinity (low buffering capacity) of sample 4 (Table 2), the addition of the optimum dosage of FS decreased the initial pH (4.5) of the water substantially. The optimum dosage of Chit and the tannin-based coagulants also had an impact on the water pH, although less significant (Fig. 12). FS achieved the best removal of DOC, tot-P, PO4-P and tot-N. The removal of DOC (76%) by FS was particularly high compared with that achieved by the other coagulants (43–57%) (Fig. 12). However, high residual Fe and SO_4^{2-} concentrations were found in the purified water (see Table 3 in Paper III). Samples treated with Chit contained higher residual DOC (due to residual organic acid used in its dissolution), but also the best removal of SS. Significant increases in concentration of tot-N (Fig. 12) and SO_4^2 (see Table 3 in Paper III) were observed in samples treated with Tan2 (due to residual coagulant). All coagulants removed phosphorus (tot-P and PO4-P) well, with FS and pDMAC achieving the highest removal rates (81–93%), followed by Chit and Tan2 (57–79%) (Fig. 12). Relatively low SS removal efficiency (<58%) was observed for all coagulants tested compared with the removal rates achieved during phases 1 and 2 (50–97%). This was probably due to the characteristics of sample 4, i.e. humic, acidic, low turbidity and low alkalinity (Table 2), which to some extent favours DOC over SS removal (Bolto and Gregory, 2007; Matilainen *et al.*, 2010).

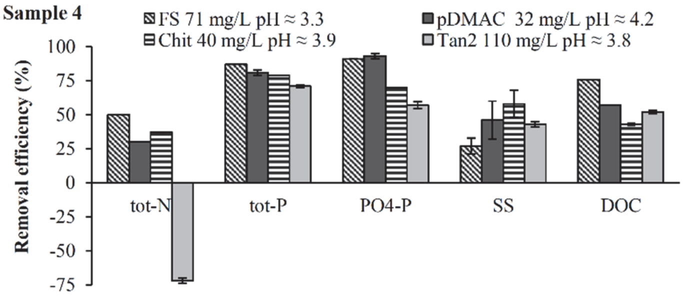


Fig. 12. Average removal efficiency (maximum and minimum values of two experimental replicates represented by error bars) achieved by the optimum dosages of coagulants at 20 °C in the purification of sample 4.

Regarding the settling characteristics of flocs formed, addition of the optimum dosage of all coagulants to sample 4 resulted in a significant increase in the initial turbidity (6.9 NTU). Pre-sedimentation turbidity of over 70 NTU was observed in samples treated with FS, while Chit- and Tan2-treated samples showed pre-sedimentation turbidity of around 35 NTU (Fig. 13). FS displayed the fastest sedimentation rates, followed by Tan2. Both achieved 80% removal of pre-sedimentation turbidity, after 4 and 6 min of settling, respectively, while Chit and pDMAC required between 8 and 11 min of settling for 80% turbidity removal. In terms of final water clarification, Chit and Tan2 were the most efficient coagulants, displaying residual turbidity close to 1 NTU (Fig. 13).

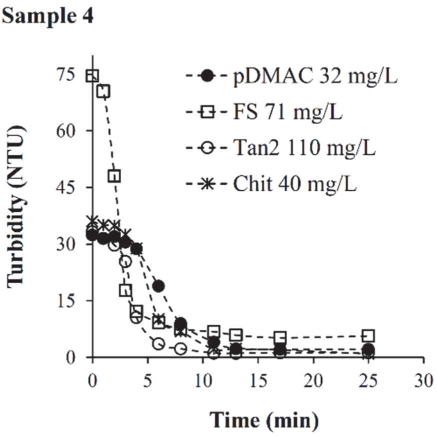


Fig. 13. Settling characteristics (removal of turbidity with time) of flocs formed by the optimum dosages of coagulants in the purification of sample 4 at 20 °C (Paper III; revised and reprinted with permission from Elsevier).

4.1.4 Overall considerations regarding coagulation of humic waters and the performance of the coagulants tested

Comparing the performance of the metal salts tested (phase 1), the better performance (lower dosage and higher removal rates) displayed by FS (Fig. 8) can to some extent be attributed to the quality of the water and to the coagulation conditions observed. Positively charged metal hydrolysis species, which are crucial for an effective coagulation process, are known to be present in a much wider pH range for iron than for aluminium salts (Duan and Gregory, 2003), including at the acidic conditions observed during the conducted experiments.

The quality of the water was also an important factor in the comparative evaluation of metal salts and organic coagulants. The humic nature of runoff water samples used throughout the optimisation studies was reflected in the SUVA values (Table 2). According to Matilainen *et al*. (2010), SUVA values between 3 and 4 indicates the presence of DOC composed of a mixture of hydrophobic and hydrophilic aquatic humics with varying MW. Furthermore, DOC fractionation analyses conducted on sample 4 (see section 4.3) showed that over 70% of DOC contained in the sample was of humic origin. In the purification of acidic and mostly humic waters, charge neutralisation/precipitation is believed to be the dominant coagulation mechanism for metal salts and organic polymers of high CD

(Kvinnesland and Ødegaard, 2004; Bolto and Gregory, 2007; Libecki, 2010). Therefore, the higher overall purification efficiency achieved by FS (Fig. 10) compared with the organic polymers tested can to some extent be attributed to its higher charge neutralisation capacity (Wei *et al.*, 2009; Matilainen *et al.*, 2010).

Regarding the performance of organic coagulants in purification of humic waters, polymers with higher CD (higher charge neutralisation capacity) are generally reported to be more effective (Bolto, 1999; Kvinnesland and Ødegaard, 2004). However, in the work presented in this thesis, there was no clear correlation between polymer CD and purification efficiency. In the purification of sample 3, pDMAC (CD 6.0 meq/g) achieved better overall performance (Fig. 10) at a lower dosage than pAmine (CD 7.0 meq/g). In the purification of sample 4, samples treated with pDMAC (CD 6.0 meq/g) contained lower overall DOC and phosphorus residuals (Fig. 12). However, higher removal of SS was achieved by Chit (CD 5.2 meq/g) and Tan2 (CD 2.2 meq/g). These findings indicate that other factors, such as MW and the distribution of the charges within the polymer molecule, interfere in the coagulation-flocculation process (Kleimann *et al.*, 2005; Gregory and Bolto, 2007).

The occurrence of the charge neutralisation coagulation mechanism was investigated by evaluating variations in colloidal surface charge (Cq) and ζ-potential with increasing dosage of coagulant to sample 4 (Fig. 14). Effective coagulation via charge neutralisation has been found to occur at ζ-potential values between -10 and +5 mV (Matilainen *et al.*, 2010). Best removal of colour and turbidity was achieved by FS dosages which produced ζ-potential and Cq values close to zero (Fig. 14a and 14b), confirming the dominance of the charge neutralisation coagulation mechanism. Based on the results obtained, a dominant charge neutralisation path could not be drawn for pDMAC, the polymer with the highest CD applied to sample 4. The residual surface charge contained in samples treated with the pDMAC optimum dosage was only slightly negative (Fig. 14b), but the resulting ζ-potential was lower (<-10 mV) than that expected for effective or dominant charge neutralisation (Fig. 14a). Although charge neutralisation could not be confirmed as the dominant coagulation mechanism for pDMAC, it is clear that it was an important factor in the destabilisation of the solution. Other mechanisms such as electrostatic patch and bridging most likely also occurred and may have played a significant role in the coagulation process.

On the other hand, charge neutralisation appears to have been the main mechanism of interaction for Chit. Samples treated by the optimum dosage of Chit showed ζ-potential values around -5 mV and charge reversal was observed within the dosage range tested (Fig. 14a). In the case of Tan2, charge neutralisation can generally be disregarded. The occurrence of bridging is also unlikely, due to the very low MW (Table 4) of the polymer (Bolto and Gregory, 2007). Electrostatic interactions such as patch coagulation can be assumed to be the main coagulation mechanism (Bolto and Gregory, 2007).

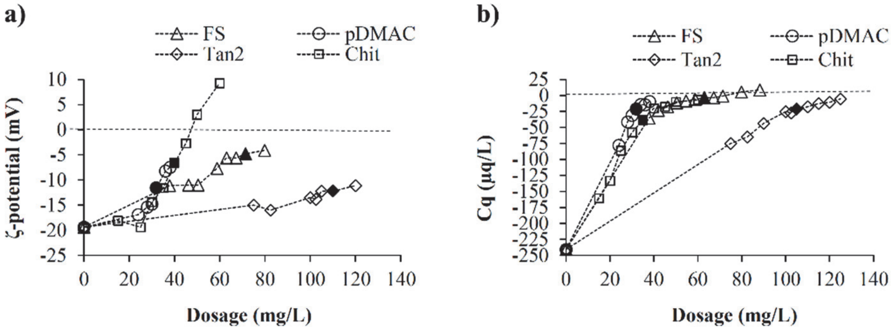


Fig. 14. Changes in ζ-potential and charge quantity (Cq) with the addition of increasing dosage of coagulant to sample 4 (optimum dosage represented by black-filled markers) (Paper III; revised and reprinted with permission from Elsevier).

Another factor which boosts the performance of FS compared with that of organic coagulants is the formation of insoluble hydrolysis products. The formation of metal hydroxide precipitates can improve the coagulation/flocculation process by increasing the number of particles in suspension, thus increasing particle collision frequency while also enabling the occurrence of adsorption destabilisation and sweep mechanisms (Bratby 2006; Bolto and Gregory, 2007; Matilainen *et al.*, 2010). This being especially beneficial for the type of natural water tested here i.e. with relatively low turbidity (Table 2).

The formation of insoluble hydrolysis products when metal salts are applied and the consequent increase in the number of particles in suspension (Packman, 1972; Amy and Chadik, 1983) can to some extent explain the overall better settling characteristics obtained by the inorganic coagulants (Figs. 9, 11 and 13). Nevertheless, good settling flocs were also formed by the organic coagulants (Figs. 11 and 13), especially by Chit and Tan2 in the purification of sample 4. It is well known that floc formation and its resulting characteristics are significantly dependent on mixing conditions applied upon and after coagulant addition (Gregory and Li, 1991; Yan *et al.*, 2009; Barbota *et al.*, 2010). The mixing parameters used throughout the optimisation studies were those identified as optimum mixing conditions for FS (pd) during phase 1 of tests (see section 4.4). Thus, it can be assumed that the mixing conditions applied to some extent favoured FS performance. Optimisation of mixing parameters to the specific requirements of the organic polymers is suggested. This could result in flocs with improved settling characteristics and an overall improvement in polymer performance. The settling rates achieved by the organic polymers were nevertheless satisfactory, and would enable good clarification results if the recommended design parameters for sedimentation units in peat extraction sites, such as surface load of 0.2–0.4 m/h, were to be applied (Turveteollisuusliitto, 2010).

An important issue regarding the chemical purification process is the environmental impacts of the residual concentrations of the added coagulants and their effect on water quality. The high dosage of FS required resulted in purified water with pH values between 3 and 4 and high residual iron concentrations (1.2–5.5 mgFe/L, see Papers I–IV). High iron concentrations (> 1 mg/L) and acidic conditions have been found to have a significant impact on the structure and function of aquatic ecosystems (Vuori, 1995; Edèn *et al.*, 1999). Evaluation of water quality monitoring data during the background study phase in this thesis work found that 75–100% of added sulphate was normally released with the purified water. Thus, for a dosage of 84 mg/L of $Fe_2(SO_4)_3$, between 45 and 60 mg/L of sulphate can potentially be released into downstream water bodies. Elevated sulphate concentrations are known to increase the mobilisation of nutrients from sediments and increase the risk of eutrophication of surface waters (Zak *et al.*, 2006).

An increase in tot-N residual concentration was consistently found in samples treated with pAmine during phase 2 of tests, which might be due to its lower molecular weight compared with pDMAC and consequently higher solubility. During phase 3 of tests, high DOC residuals were found in Chit-treated samples due to residual acetic acid used in product dissolution. This might be avoided by the dissolution of Chit in other acids, e.g. hydrochloric or glutamic acid (Bratskaya *et al.*, 2004). Chemically modified water-soluble chitosan products have also been successfully studied (Yang *et al.*, 2011). During phase 3, high residual coagulant levels were also found in Tan2-treated samples, most likely as a result of overdosing in terms of colour removal. Throughout the optimisation studies, a combined requirement of colour and turbidity removal was imposed. During dosage requirement evaluations for Tan2 (Fig. 6), satisfactory colour removal was obtained at a substantially lower dosage than turbidity removal.

Further research is required to determine the residual concentrations resulting from the use of synthetic and natural organic polymers as primary coagulants and their potential impact on the environment. Existing studies mostly report impacts related to residual concentrations resulting from the lower dosage required when polymers are used as flocculant aid chemicals (Harford *et al.*, 2011).

Overall, FS was the best performing coagulant. Nevertheless, the organic polymers tested demonstrated satisfactory overall performance, with purification rates mostly inside the required range for chemical purification of peat extraction runoff (COD 60–80%, SS 50%, tot-N 30–50% and tot-P 60–90%; Wichmann, 2015). Furthermore, Chit and the synthetic organic polymers required substantially lower dosages than FS and had small or no effects on the pH of the water.

4.2 Effect of water pH on purification (I–IV)

The pH of peat extraction runoff water mainly fluctuates within between 4.5 and 7.0 (Table 5). Thus, the pH variations tested (4.5–6.5) reflected real operating conditions. The influence of pH on purification efficiency was evaluated for all test coagulants (see Papers I–IV). The results presented here show the influence of pH on the performance of (i) synthetic polymers and FS in the purification of sample 3 and (ii) natural and synthetic polymers and FS in the purification of samples 4 and 5.

To evaluate the influence of water pH on the performance of FS and synthetic organic polymers, the pH of sample 3 was increased from its natural value of 4.5 to 5.5 and subsequently to 6.5 (phase 2 of tests). The following dosages were selected from the optimum range identified for each coagulant at different pH, taking into consideration the removal of colour and turbidity:

- pH 6.5: pAmine 25 mg/L, pDMAC 16 mg/L, FS 84 mg/L.
- pH 5.5: pAmine 20 mg/L, pDMAC 16 mg/L, FS 59 mg/L.
- pH 4.5: pAmine 15 mg/L, pDMAC 10 mg/L, FS 50 mg/L.

Significant lower dosages were required for equivalent removal of colour and turbidity in the purification of lower pH samples. When the identified optimum dosage of synthetic organic polymers and FS was applied to sample 3 (pH 4.5, 5.5 and 6.5), comparable removal rates of TOC, SS, tot-P, PO4-P and tot-N were achieved at all pH levels (Fig. 15). However, as mentioned, significantly lower dosages were applied in the purification of samples with lower initial pH.

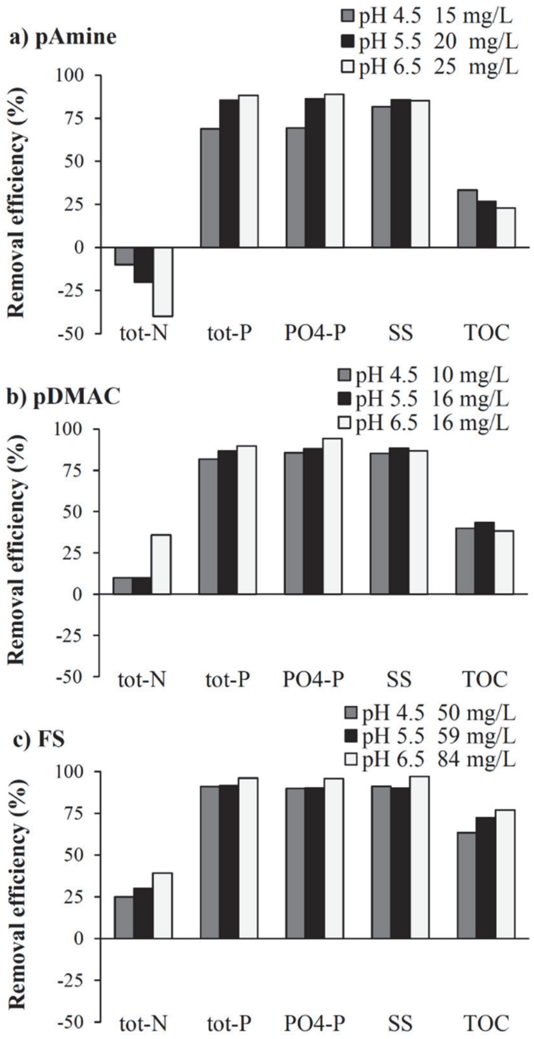


Fig. 15. Removal efficiency (%) achieved by the optimum dosage of coagulants in the purification of sample 3 at initial pH 4.5, 5.5 and 6.5 and 20 °C (pH adjustment by NaOH addition) (Pape II; revised and reprinted with permission from Taylor & Francis).

A similar trend was observed when the influence of water pH on the performance of FS, pDMAC and natural polymers was investigated during phase 3 of tests. Lower dosages were required in the purification of sample 4 (pH 4.5) than sample 5 (pH 6.5). The optimum coagulant dosages identified were:

- Sample 4 pH 4.5: FS 71 mg/L, pDMAC 32 mg/L, Tan2 110 mg/L, Chit 40 mg/L.
- Sample 5 pH 6.5: FS 80 mg/L, pDMAC 52 mg/L, Tan2 170 mg/L, Chit 50 mg/L.

When the identified optimum dosages of coagulants were added to samples 4 (pH 4.5) and 5 (pH 6.5), during phase 3 of tests, equivalent removal of phosphorus and organic matter was observed (Fig. 16). Furthermore, the removal of SS by organic coagulants was generally higher in the purification of the lower pH sample (Fig. 16b–16d), despite, the lower dosages applied in the purification of sample 4.

The pH at which coagulation takes place is known to have a significant effect on coagulation and flocculation results. In natural waters, decreasing the water pH decreases the ionisation of carboxylic and phenolic functional groups of humic acids, resulting in a net decrease in negative charges and giving humic substances more hydrophobic characteristics (Bolto and Gregory, 2007). Besides influencing the physical and chemical characteristics of pollutant substances, pH also has a direct impact on coagulant properties and on the way it interacts with water and other substances (Bolto and Gregory, 2007; Slavik *et al.*, 2012). At acidic pH, the hydrolysis species of metal salt coagulants are believed to be of a polymeric and more positive nature, thus improving their charge neutralisation capability (Bratby, 2006). According to the product suppliers, the cationic charges contained in the pAmine, pDMAC and tannin polymers tested are the result of quaternary ammonium groups, and thus their CD should not be pH-dependent. Nevertheless, in the case of pDMAC it has been suggested that the non-polar characteristics of its molecules facilitate their interaction with the more hydrophobic humic substances in acidic pH conditions (Kvinnesland and Odegaard, 2004). The cationic charge of Chit is due to the presence of amine groups in the polymer chain. The protonation of these groups at low pH imparts high cationic CD to the polymer, which decreases significantly at pH ≥ 6 (Renault *et al.*, 2009). Therefore, at lower pH, stronger interactions between the positively charged groups of Chit and negatively charged pollutants can be expected. As previously described, in the purification of acidic and humic waters, charge neutralisation is believed to be the dominant coagulation mechanism (Kvinnesland and Odegaard, 2004; Kleimann *et al.*, 2005; Bolto and Gregory, 2007). Thus, it follows that at lower pH, lower coagulant dosages were required for effective coagulation (Figs. 15 and 16).

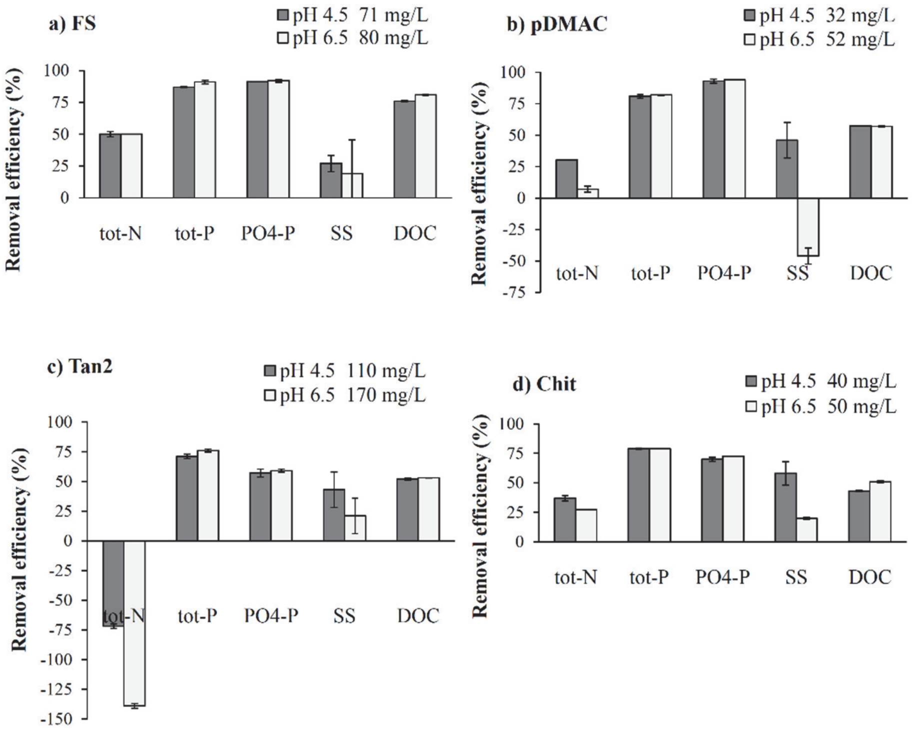


Fig. 16. Average removal efficiency (%) achieved by the optimum dosage of coagulants (maximum and minimum values of two experimental replicates represented by error bars) at 20 °C in the purification of sample 4 (pH = 4.5) and sample 5 (pH = 6.5).

4.3 Effect of coagulant type and pH on DOC fractions removed (III)

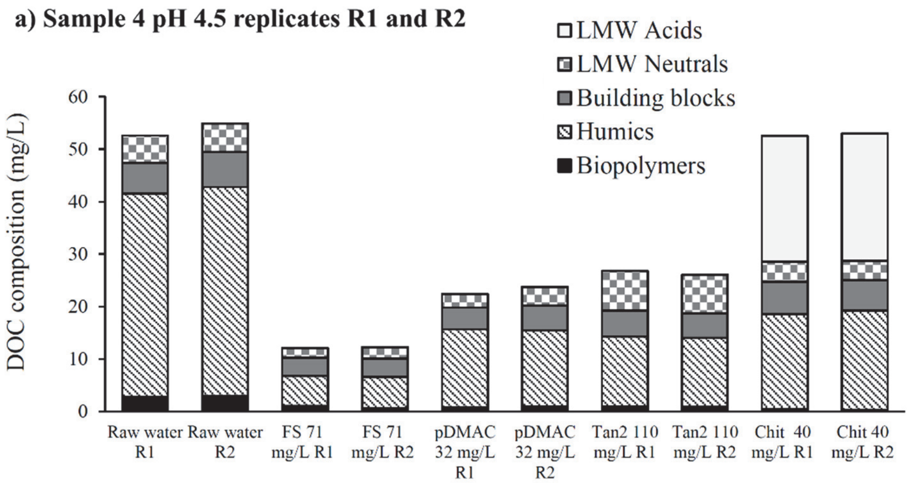
In order to evaluate the influence of coagulant type and pH on DOC removal, or more specifically the removal of different fractions within the DOC pool, samples 4 and 5 were treated with the optimum dosages of FS, pDMAC, Chit and Tan2 identified during phase 3 of tests. The purified water was then analysed using LC-OCD-OND techniques.

According to the LC-OCD-OND analysis, about 5% of the DOC contained in samples 4 and 5 (~2.8 mg/L) was in the form of biopolymers (Fig. 17). Biopolymers in this context are hydrophilic, high MW and non-ionic substances (Huber *et al.*, 2011). All coagulants removed biopolymers well, with higher removal rates observed in the purification of sample 4 (low pH; Fig. 17a). This was particularly evident for Chit which removed 85% of biopolymers in the purification of sample 4 and 55% in the purification of sample 5. The HS fraction, consisting mainly of humic and fulvic acids, made up the bulk of the DOC contained in the raw water samples (~41 mg/L). In general, the HS fraction was more effectively removed by FS (85–91%), with Tan2 showing the best removal (66–72%) among the organic coagulants (Fig. 17).

The building blocks fraction is composed of breakdown products of HS. This fraction has previously been found not to be effectively removed by coagulation-flocculation (Bolto *et al.*, 1999; Huber *et al.* 2011). Interestingly, some reduction was observed here, especially when FS was applied (~46%). The raw water samples did not contain LMW acids. However, around 30–45% of residual DOC contained in Chit-treated samples was composed of LMW acids (Fig. 17). This increase in LMW acid concentrations can be attributed to the presence of acetic acid, which was used in dissolution of the chitosan product.

The LMW neutrals fraction of NOM contains alcohols, aldehydes, ketones, sugars and amino acids (Huber *et al.*, 2011). Around 4–5 mg/L of LMW neutrals were present in the raw water samples and these were satisfactorily removed from sample 4 (pH 4.5; Fig. 17a), with FS being the most efficient coagulant (62%). The concentration of LMW neutrals in samples treated with Tan2 was higher than that initially found in the raw water samples (Fig 17). The observed increase was due to residual coagulant. Tan2 is composed of very low MW polymeric chains, which may display neutral characteristics in post-coagulation conditions (Fig. 14b). This possibility was confirmed by the increased tot-N concentration and the occurrence of late eluting organic-bound (LMW neutrals) nitrogen found in Tan2-treated samples (see Table 4 in Paper III).

The higher MW fractions (biopolymers and HS) were more efficiently removed by all coagulants tested, confirming previous findings (Bolto *et al.*, 1999; Korshin *et al.*, 2009). The significantly higher removal rates shown by FS highlight the importance of charge neutralisation in DOC removal by coagulation-flocculation. However, the good HS removal rates achieved by Tan2 shows that charge neutralisation should not be considered the only effective mechanism of HS removal.



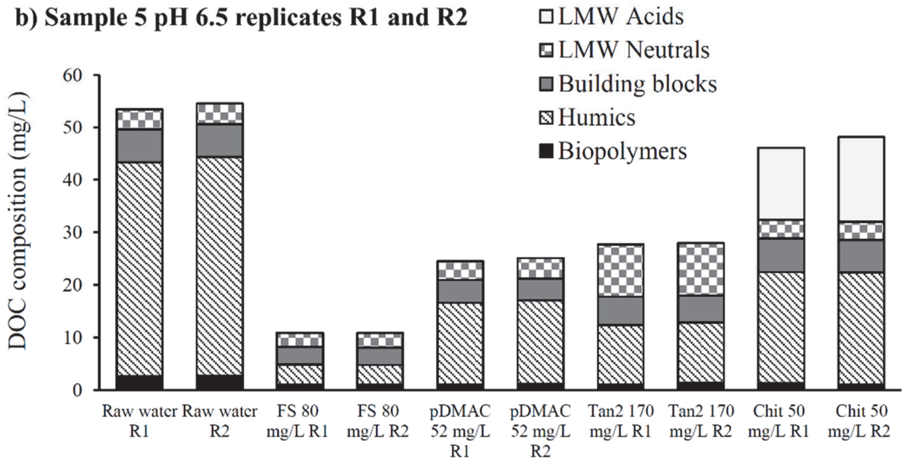


Fig. 17. Concentration of dissolved organic carbon (DOC) fractions produced as a results of LC-OCD-OND fractionation of raw (sample 4 and sample 5) and treated water samples (2 replicates, R1 and R2) (Paper III; revised and reprinted with permission from Elsevier).

4.4 Effect of provided mixing on purification (I)

Mixing applied upon and after coagulant addition is known to have a significant effect on purification results (Yan *et al.*, 2009). Most studies reporting the influence of mixing on coagulation and flocculation processes relate their results to pre-dissolved or liquid coagulants (e.g. Rossini *et al.*, 1999; Yan *et al.*, 2009). Due to the fact that solid iron salts are normally used in the purification of peat extraction runoff water, evaluation of the influence of mixing on the performance of aluminium and iron-based coagulants in solid and pre-dissolved form was conducted (I). Optimisation of mixing parameters suitable for the metal salt coagulants tested was performed using the one factor-at-a-time optimisation method (Cochran and Cox, 1957).

Varying the mixing time and speed during the coagulation (fast) and flocculation (slow) stages of the purification process had a significant influence on the removal efficiencies achieved. The findings obtained regarding the influence of mixing on the coagulation or fast mixing stage mostly agree with those of previous studies (Rossini *et al.*, 1999; Kan *et al.*, 2002; Yan *et al.*, 2009). The removal of dissolved substances such as organic matter was only slightly affected by the intensity and duration of the rapid mixing stage, while the removal of SS appeared to decrease with increasing mixing time and increase with increasing mixing intensity until a critical value was reached. On the other hand, mixing applied during the flocculation stage had a more significant influence on results, especially on the removal of SS. The observations made on the characteristics of the flocs formed during the flocculation stage generally comply with widely reported characteristics in the literature (AWWA, 1990; Bratby, 2006; Zhan *et al.*, 2011). Low velocity gradients of less than 20 (s^{-1}) and long retention times of 25 min produced large but light flocs, which did not settle well. Short retention times of 5 minutes and higher mixing intensity produced very small flocs, especially in the case of solid coagulants, which also remained in suspension.

The presented results (Fig. 18) represent a comparison between the purification efficiency obtained in the treatment of water sample 1 when *optimum* (opt.) and *most unsatisfactory* (uns.) mixing parameters identified during the optimisation stage were applied (Table 8). In general, the lowest removal efficiency weas observed when either short mixing time or low mixing speed was utilized during the flocculation stage. Furthermore, significant differences were found between the mixing requirements or optimised mixing conditions for coagulants dissolved prior to application and coagulants dosed directly in solid form (Table 8).

Table 8. Identified optimum and most unsatisfactory mixing parameters for the coagulants tested, based on turbidity and colour removal (Paper I; reprinted with permission from Elsevier).

Coagulant	Mixing	Dosage	Fast mixing time (s)	Fast mixing speed (rpm)	G (s-1)	Slow mixing time (min)	Slow mixing speed (rpm)	G (s-1)
Alum sol	opt.	70	10	400	756	25	70	55
Alum sol	uns.	70	60	400	756	15	20	9
FS sol	opt.	60	10	400	756	25	70	55
FS sol	uns.	60	60	400	756	5	70	55
Alum pd	opt.	70	10	100	95	25	50	34
Alum pd	uns.	70	60	400	756	5	50	34
FS pd	opt.	60	10	300	491	25	50	34
FS pd	uns.	60	60	400	456	5	50	34

For solid coagulants, low mixing speed of 20 rpm, even when combined with mixing times inside the optimum range (15–25 min), produced removal efficiencies up to 80% lower than at the optimum speed of 70 rpm (Fig. 18). Short flocculation mixing times of 5 minutes appeared to have an even greater influence on purification, especially in the removal of SS, where the fluctuations in removal efficiency compared with optimum mixing conditions were greater than 100% (Fig. 18). The mixing requirements or the optimum mixing conditions for the pre-dissolved coagulants differed from those identified for the solid coagulants (Table 8). However, low mixing speeds and short mixing times in the flocculation stage also produced significant fluctuations in the removal efficiencies of pre-dissolved coagulants (Fig. 18c and 18d); nevertheless, the fluctuations were less pronounced than those observed for solid metal salts (Fig. 18a and 18b).

According to the results, adequate mixing conditions during the flocculation stage is a crucial factor affecting the purification results, especially for solid coagulants. By introducing mixing during the flocculation stage in existing treatment facilities, it should be possible to achieve improvements in treatment efficiency, especially regarding the removal of SS. Based on the observations made during this thesis work, an additional study (Mohammadighavam *et al.*, 2015b) was conducted (not included in this thesis) where the introduction of a hydraulic mixing structure to the layout of existing treatment facilities was evaluated. Optimised mixing parameters (velocity gradient and retention time) identified here were used in the additional study as input in building a turbulent three dimensional (3D) computational fluid dynamic (CFD) model. The model was then utilised to develop, evaluate, and optimise a hydraulic mixing structure that could provide optimum mixing parameters. The proposed design was built by Vapo Oy in a selected extraction site and is now being monitored and evaluated.

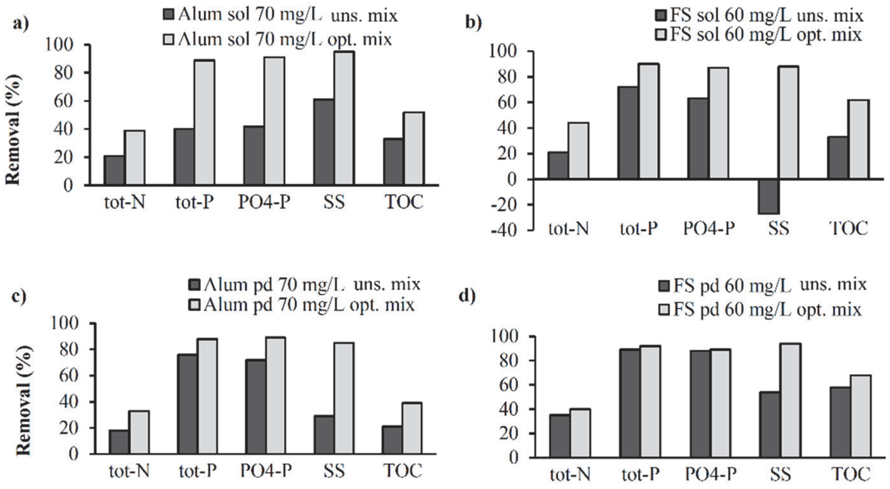


Fig. 18. Comparison of removal efficiency achieved in the purification of water sample 1 (pH 6.5) following application of the optimum (op. mix) and unsatisfactory (uns. mix) mixing parameters (Paper I; revised and reprinted with permission from Elsevier).

4.5 Effect of water temperature on purification (I and II)

To evaluate the influence of temperature on the purification process, the temperature of sample 1 was decreased from 20°C (normal test temperature) to 5 °C (phase of 1 tests) while the temperature of sample 3 was decrease to 2°C (phase 2 of tests). Sample 1 was treated with the optimum dosage of Alum and FS (solid and pre-dissolved), while sample 3 was treated with optimum dosage of FS (liquid) and the synthetic organic polymers, pDMAC and pAmine.

The decrease in water temperature had an overall negative effect on purification efficiency achieved by all coagulants in the treatment of both water samples (Fig. 19). The magnitude of this influence depended on: (i) the coagulant type, (ii) its physical form and applied dosage and (iii) the contaminant substances being removed. In general, low temperature had a small influence on the removal of phosphorus fractions, nitrogen and organic matter, but, the removal of SS was significantly affected (Fig. 19). The detrimental effects of temperature on SS removal were particularly significant when solid metal salts were applied (Fig. 19a and 19b).

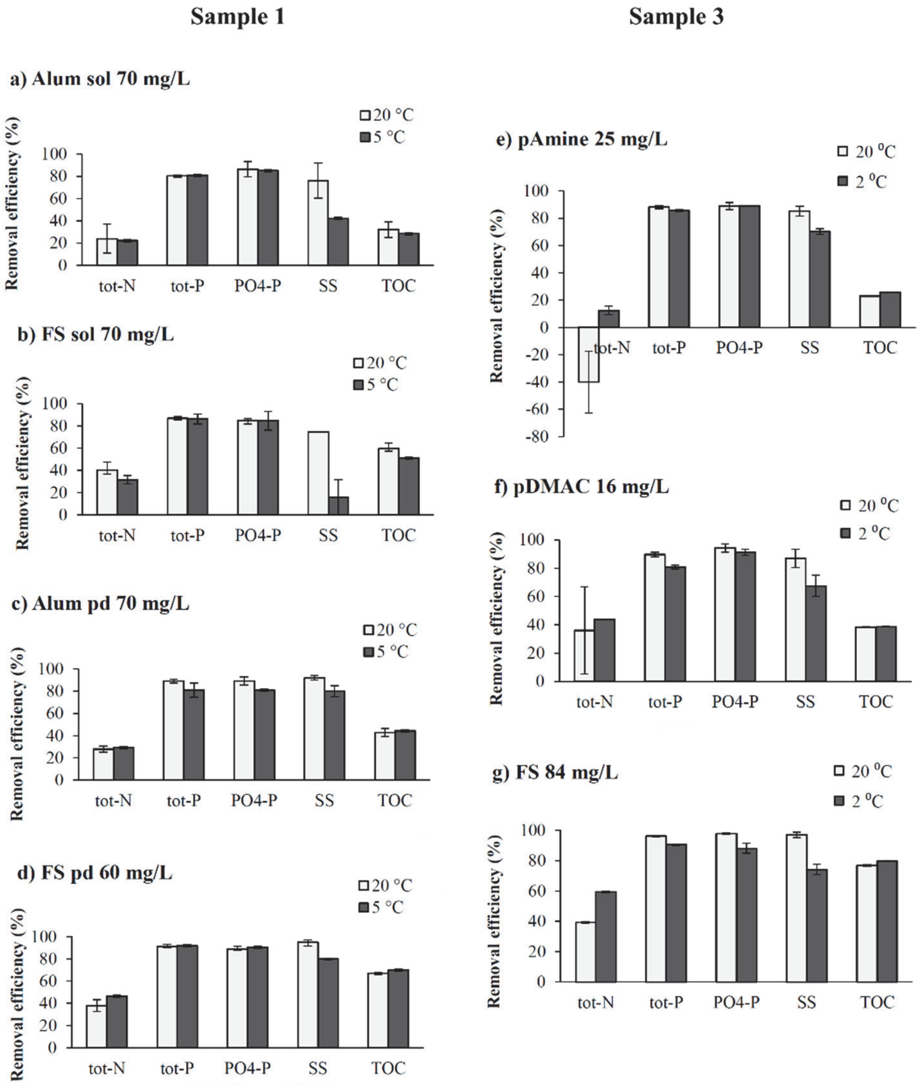


Fig. 19. Influence of water temperature on the purification efficiency achieved by metal salts and synthetic organic coagulants (maximum and minimum values of experiment replicates represented by error bars) in the treatment of sample 1 (a–d, n = 3) and sample 3 (e–g, n = 2) (Paper I, revised and reprinted with permission from Elsevier; Paper II revised and reprinted with permission from Taylor & Francis).

Low temperature is known to affect coagulation and flocculation by altering coagulant solubility, increasing water viscosity and hindering charge neutralisation reactions, especially the subsequent particle aggregation process (Kang and Cleasby, 1995; Xiao *et al.*, 2008, 2009). The low influence of temperature in the removal of dissolved substances obtained during this study (Fig. 19) agrees with previous findings that the most significant influence of low temperature occurs during the flocculation and sedimentation stages of the purification process (Kang and Cleasby, 1995; Xiao *et al.*, 2008), resulting in a significant impact on floc characteristics and on the removal of SS. Visual observations made during the experiments identified clear differences in floc characteristics between coagulants applied in solid, pre-dissolved and liquid form, which points to a direct influence of temperature on the solubility of the coagulants. To the best of my knowledge, the influence of temperature on the coagulation mechanisms of organic polymers has not previously been studied in detail. According to the results, based solely on the removal efficiencies achieved, it appears that temperature has a similar effect on the performance of organic coagulants and metal salt coagulants (Fig. 19).

The negative influence of temperature on SS removal was observed in more detail during settling experiments (Fig. 20). In the purification of sample 1, all coagulants required between 50 and 200% longer settling times to reach 80% removal of pre-sedimentation turbidity at 5°C than at 20°C, with the solids coagulants being the most affected. In addition, samples treated with solid coagulants showed 5–15% higher turbidity values at the end of the settling period compared with the pre-dissolved coagulants (Fig. 20a and 20b). An delay in the settling rates were also observed in the purification of sample 3 at 2°C, with 50–100% longer times needed for 80% turbidity removal (Fig. 20c–20e).

The impact of temperature on the chemical purification process is an important factor in cold climate regions, where water temperatures can remain below 10 °C for more than 6 months of the year. The addition of a flocculant aid polymer has been found to decrease the required dosage of primary coagulant and to significantly improve the settling characteristics of the flocs formed (Lee *et al.*, 2001; Aguilar *et al.*, 2005). Therefore, implementation of a dual chemical coagulation method whereby a flocculant aid polymer is introduced after the primary coagulant to enhance the flocculation and sedimentation processes, should be explored at sites where year-around chemical purification is required.

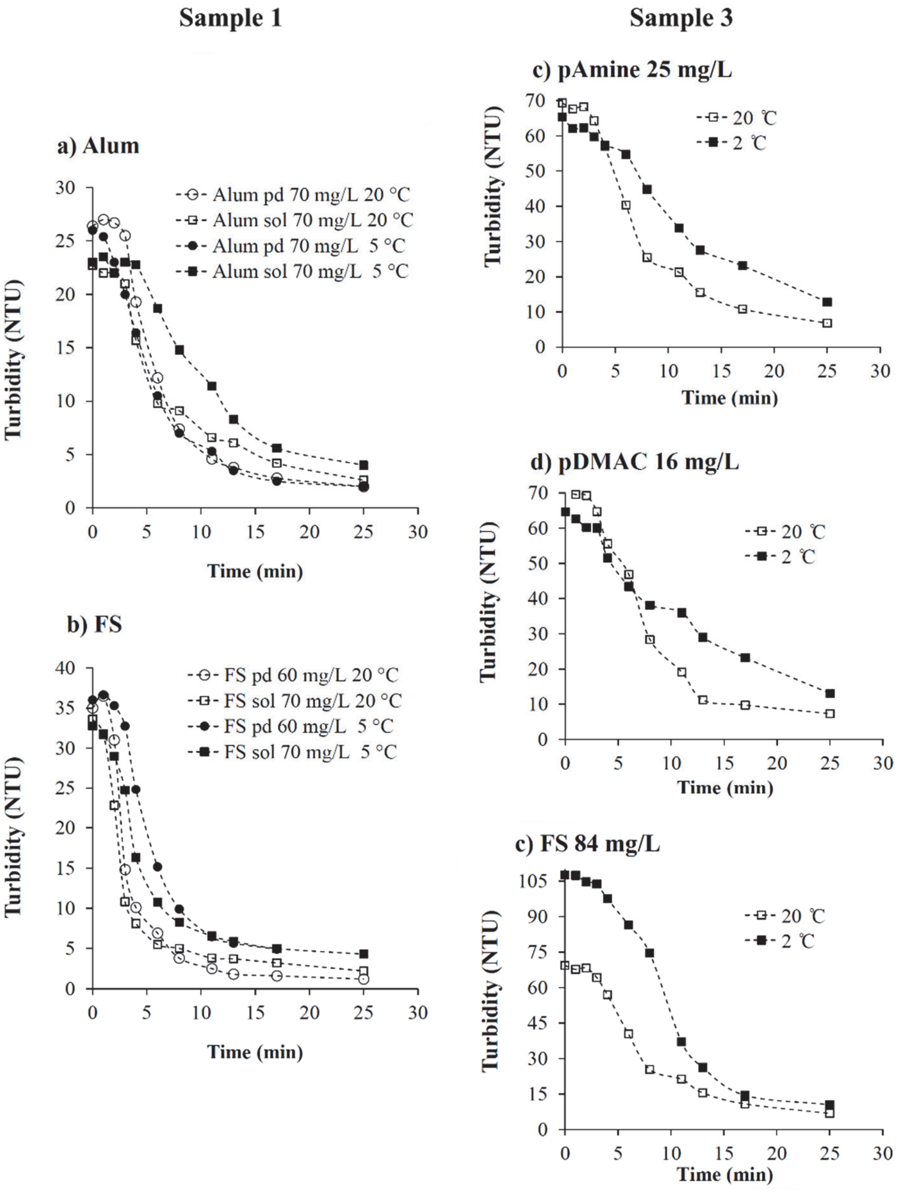


Fig. 20. Influence of water temperature on the settling characteristics of flocs formed (removal of turbidity with time) in the purification of sample 1 (a, b) and sample 3 (c–e).

4.6 Influence of water quality variations on purification efficiency (IV)

To evaluate the influence of variations in water quality on purification efficiency, water quality monitoring data were used to determine typical ranges of concentration fluctuations in water quality indicators, referred to here as ‘factors’ (DOC, SS and pH; Table 5). A 2^4 factorial design was applied in the design of the laboratory experiments. Natural water samples were used to create eight sub-samples containing the combination of identified low and high concentration levels of the water quality factors (Fig. 7). Dosage requirement tests revealed the high and low FS dosages needed to treat such samples. The eight sub-samples were then treated using high and low coagulant dosages resulting in 16 experimental runs which were conducted in triplicates.

Overall purification results

Residual concentrations of a series of water quality parameters found in the treated samples are presented in Table 9. The focus is on the selected response variables of the experimental design, i.e. the DOC, SS and tot-P concentrations, which were used in the evaluation of results using ANOVA and factor effect calculations.

In general, the residual concentrations of DOC, SS and tot-P found in the treated samples were substantially influenced by the initial DOC concentration of the water (Table 9). For samples with high initial DOC (70 mg/L) and to which a low coagulant dosage (35 mg/L) was applied (Table 9; samples a, ab, ac, abc), distinct signs of under-dosing such as highly negative Cq values and high residual concentrations of DOC, SS and tot-P were observed. Satisfactory purification levels were achieved for samples treated with a high coagulant dosage (100 mg/L). Dosage requirement was therefore clearly dependent on the initial DOC concentration of the samples.

Table 9. Water quality characteristics of treated samples (response variables: average of n=3 replicates ± standard deviation (st.dev), other measured parameters: average of n=3 replicates) (Paper IV; reprinted with permission from Elsevier).

	Response variables (evaluation of purification efficiency)			Other measured parameters					
Treatment combinations	DOC (mg/L) ±st.dev	SS (mg/L) ±st.dev	tot-P (µg/L) ±st.dev	PO_4-P (µg/L)	tot-N (µg/L)	Purified water pH	UV_{254} abs. (1/cm)	Fe (mg/L)	Cq (µeq/L)
(1)	4.1 ±0.0	2.7 ±0.2	3.7 ±0.6	2*	217	3.6	0.204	3.3	-3.1
a	46.7 ±2.1	17.0 ±2.6	69.3 ±0.6	23	1200	3.7	3.003	8.3	-124
b	3.4 ±0.1	2.0 ±0.1	4.0 ±1.0	2*	247	3.6	0.220	3.2	-2.8
ab	36.4 ±1.6	33.0 ±2.6	84.3 ±2.1	41	1200	3.7	2.743	9.0	-88
c	3.6 ±0.3	2.1 ±0.3	5.3 ±0.6	2*	170	4.0	0.153	1.6	-3.7
ac	51.3 ±0.6	7.0 ±1.3	73.0 ±2.0	20	1267	5.5	3.002	8.3	-284
bc	3.0 ±0.3	1.3 ±0.1	3.3 ±0.6	2*	153	3.9	0.111	1.7	-3.1
abc	49.0 ±1.0	23.7 ±1.2	89.0 ±2.6	33	1300	5.4	2.780	9.4	-234
d	3.5 ±0.1	16.7 ±0.6	3.7 ±0.6	2*	207	3.3	0.445	12.0	-0.8
ad	16.4 ±2.1	6.2 ±0.2	12.7 ±0.6	2*	450	3.3	0.758	8.4	-3.9
bd	3.0 ±0.1	14.3 ±1.2	4.3 ±0.6	2*	247	3.2	0.501	11.7	-1.9
abd	13.7 ±0.6	5.1 ±0.5	12.3 ±2.3	3	370	3.3	0.648	9.1	-3.0
cd	3.0 ±0.2	9.4 ±0.3	4.3 ±1.2	2*	160	3.3	0.338	8.3	-2.2
acd	13.0 ±1.0	4.6 ±0.2	12.0 ±1.0	2*	443	3.6	0.462	4.7	-8.0
bcd	2.6 ±0.2	9.5 ±0.5	4.0 ±1.7	2*	163	3.3	0.358	8.6	-0.8
abcd	10.0 ±0.0	3.4 ±0.5	13.3 ±5.1	2*	370	3.6	0.365	5.0	-5.1

* Method detection limit.

Evaluation of factor effects – Statistical analysis

The results of factors effect calculations and F-statistics of the ANOVA evaluations for the response variables DOC, SS and tot-P are presented in Table 10.

DOC residuals: The magnitude of factor A (DOC) effect (26) on DOC residual concentration was strong and in the positive direction (Table 10), meaning that, the residual DOC concentration in the treated samples generally increased as factor A varied from its low to its high level. The factor D (Dos) effect was also strong (-17) but in the negative direction. As factor D varied from its low to its high level, the residual DOC concentration generally decreased. A strong interaction effect AD (-16) between initial DOC concentration and applied dosage was also observed. The F-statistics from ANOVA confirmed the significant influence of factor A, factor D and the interaction effect AD on DOC residuals. However, ANOVA also showed that the influence of all other factors and factor interactions was statistically significant at the 95% confidence interval (Table 10).

SS residuals: The SS residual concentrations found in the treated samples were mostly influenced by the interaction effect AD between the initial DOC concentration of the water and the coagulant dosage applied (Table 10). F-statistics from ANOVA revealed that, while most individual factor effects were significant, the interactions BC, CD, ABC, BCD and ABCD were not significant at 95% confidence interval (Table 10).

tot-P residuals: The influence of the individual factors A and D and the interaction between these two factors was critical for the tot-P residual concentration. The magnitude of the factor A effect (42), factor D effect (-33) and the interaction effect AD (-33) was very strong. According to the magnitude of factor effects and p-values from the F-statistics (ANOVA), factor C (pH) had the least significant influence on tot-P residual concentration (Table 10). Furthermore, regarding tot-P residual concentration, all interaction effects containing factor C were not significant at 95% confidence interval (Table 10).

Table 10. Magnitude of factor effects and significance of factor effects (ANOVA, 95% confidence interval) on the response variables (DOC, SS and tot-P) (Paper IV; revised and reprinted with permission from Elsevier).

		DOC residual		SS residual		tot-P residual	
		Magnitude of factor effect (OC)	ANOVA p-value F statistics	Magnitude of factor effect (OC)	ANOVA p-value F statistics	Magnitude of factor effect (OC)	ANOVA p-value F statistics
Factor and factor interactions	A	26	0.000	5	0.000	42	0.000
	B	-3	0.000	3	0.000	4	0.000
	C	1	0.001	-5	0.000	1	0.027
	D	-17	0.000	-2	0.000	-33	0.000
	AB	-2	0.000	4	0.000	4	0.000
	AC	2	0.000	-1	0.001	1	0.098
	AD	-16	0.000	-13	0.000	-33	0.000
	BC	1	0.001	0	0.282	0	0.878
	BD	1	0.002	-4	0.000	-4	0.000
	CD	-3	0.000	1	0.045	-1	0.053
	ABC	1	0.002	0	0.487	1	0.173
	ABD	1	0.006	-4	0.000	-4	0.000
	ACD	-3	0.000	3	0.000	-1	0.098
	BCD	-1	0.001	0	0.519	0	0.646
	ABCD	-1	0.001	0	0.185	0	0.878

Evaluation of factor effects – Graphical representation

According to the method used for OC calculations, when strong interaction effects occur, the magnitude of the individual factor effects may be inflated (Montgomery, 2006). Therefore, graphical representations of the interaction effects (Figs. 21, 22 and 23) were used to further clarify the results obtained.

DOC residuals: Graphical representation of factor effects revealed that the strongest and most significant effect on DOC residuals came from factor A (DOC) (Fig. 21c). It is clear that although the influence of applied dosage (D) was strong, its influence was substantially dependent on the initial DOC concentration of the sample, i.e. dosage had a significant impact on the residual DOC found in the purified water only for samples with high initial DOC concentration (Fig. 21d–21g). The influence of initial water pH (C) and SS concentration appeared to be small and only slightly dependent on the level of factor A (DOC) (Fig. 21a and 21b).

In agreement with previous findings (Jiang and Wang, 2009), lower DOC residuals were found in samples with higher initial SS concentration. (Fig. 21g). The presence of SS (up to a limiting concentration) does not necessarily result in an increase in dosage requirements and, as seen in our results, it can improve DOC removal. Higher particle concentrations, as previously discussed, increase collision frequency, improving floc aggregation rates and resulting in larger flocs with better settling characteristics, which in turn leads to higher purification efficiency (Packman, 1972; Amy and Chadik, 1983).

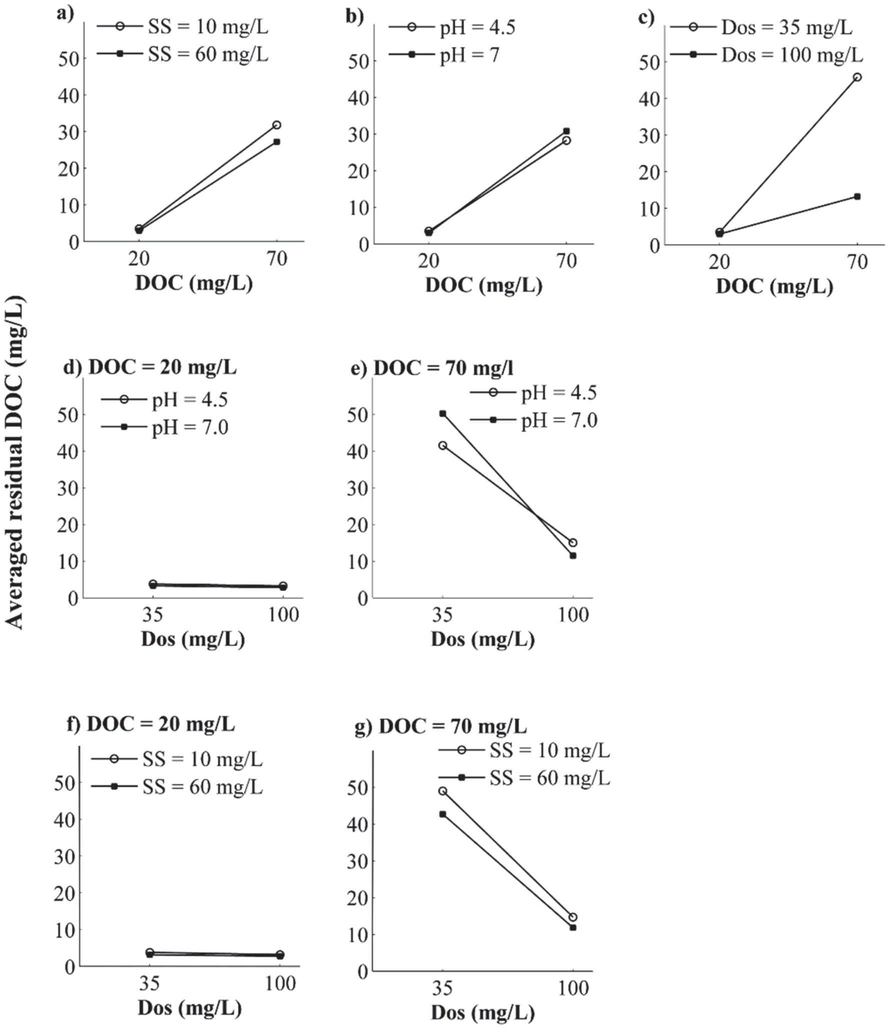


Fig. 21. Most significant factor interaction effects on the response variable residual dissolved organic carbon (DOC): Two-factor interaction effects (a–c) and three-factor interaction effects (d–g) (Paper IV; reprinted with permission from Elsevier).

The significant influence of pH on the purification process and especially on DOC removal is described in sections 4.2 and 4.3. However, the results obtained during this phase of tests showed that variations in pH had a rather small influence on DOC residuals. This limited influence of pH can be linked to the low alkalinity of the water samples tested, coupled with the fact that the pH levels in both samples were at the neutral to acidic pH scale, which resulted in very similar coagulation pH ($3.5 < pH < 5$).

SS residuals: Regarding the influence of factor interactions on the response variable SS residuals, the graphical representation also revealed a strong interaction between factors A (DOC) and D (Dos) (Fig. 22d). In addition, it revealed that the initial DOC concentration and applied dosage had an antagonistic influence on SS concentration. Lower SS residuals were observed for lower dosages at low initial DOC concentration, but for higher dosages at high initial DOC concentration. This strong antagonistic interaction effect between DOC and coagulant dosage can to some extent be explained by the occurrence of over-dosage or under-dosage during the purification process. High residual iron concentrations (Table 10) were found in the treatment combinations d, bd, cd and bcd, pointing to over-dosage. Another finding indicating over-dosage was the positive Cq values observed in replicates of the four treatment combinations listed, a clear sign of charge reversal. The occurrence of charge reversal and a possible increase in iron hydrolysis species in suspension due to over-dosage (Duan and Gregory, 2003; Sansalone and Kim, 2008) can explain the observed increase in the residual SS concentration of the samples (Fig. 22f). During under-dosing, observed for treatment combinations a, ab, ac and abc, the influence of factor B (initial SS) on the residual SS of the sample increased (Fig. 22g). Basically, an insufficient amount of coagulant was added to efficiently precipitate the DOC and SS present in the sample. Furthermore, the use of below-optimum dosage is known to result in the formation of micro-flocs, which do not sediment well, thus increasing the residual SS and iron concentration of the samples.

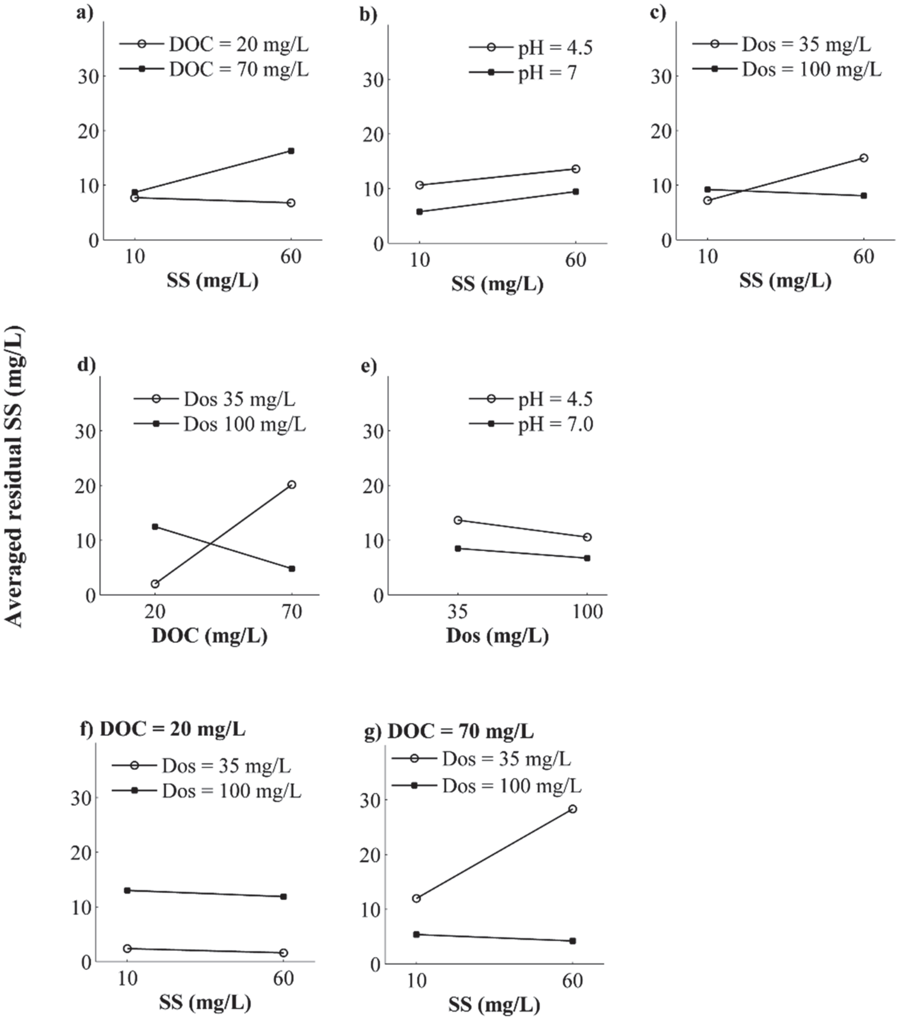


Fig. 22. The most significant factor interaction effects on the response variable residual suspended solids (SS): Two-factor interaction effects (a–e) and three-factor interaction effects (f–g) (Paper IV; reprinted with permission from Elsevier).

tot-P residuals: Graphical representation of factor effects on tot-P residuals (Fig. 23) revealed that the dosage applied greatly affected tot-P removal, but only for samples with high initial DOC concentration (Fig. 23c, 23f and 23g). Thus the magnitude of the factor D (Dos) effect was clearly dependent on the level of factor A (DOC). The graphical representation also showed the higher order interaction between factors A, B and D. Higher tot-P residual concentration was found in samples with higher initial SS (B), but only for the treatment combinations where a low dosage (D) was applied to samples with a high initial DOC (A) (Fig. 23f and 23g).

Regarding the effect of factor B (the initial SS concentration of the samples), it can be assumed that it was mainly due to the effect it had on the initial tot-P concentration of the water. Higher initial SS resulted in higher initial tot-P concentration (Table 6). Higher SS concentrations led to higher residual SS at low coagulant dosages, which consequently resulted in higher particulate phosphorus in the treated samples. As for the low influence of pH on the residual concentration of tot-P, it can also be explained (as can the influence of pH on the DOC residuals observed) by the similarly acid pH characteristics of treated samples (Table 10), which resulted in coagulation pH of a similar nature. The removal of phosphorus from humic waters is said to be enhanced at acidic (<5) pH values and is linked to the formation of humic acid-metal-phosphate complexes (Cheng *et al*., 2004). For the 16 experimental runs performed in this thesis, treated samples which contained low residual DOC also contained very low residual PO4-P concentration (Table 10), which further explains the relationship between DOC and tot-P removal.

Overall, it can be concluded that the initial DOC concentration of the raw water samples and its interactions with the coagulant dosage exerted the most significant influence on the residual concentrations of DOC, SS and tot-P. However, the influence of coagulant dosage was only significant for samples with high initial DOC concentration. The variations applied to the factors SS and pH appeared to affect the removal of DOC, SS and tot-P only slightly. Nevertheless, high SS concentration led to lower DOC residuals at all dosages applied and lower DOC residuals were observed in samples with high initial pH when high coagulant dosages were applied. For this type of diffuse runoff, i.e. of a humic and acidic nature, coagulant dosage should be adjusted according to variations in DOC concentration to ensure an efficient purification process where other substances of concern, such as SS, tot-P, etc., are also efficiently removed.

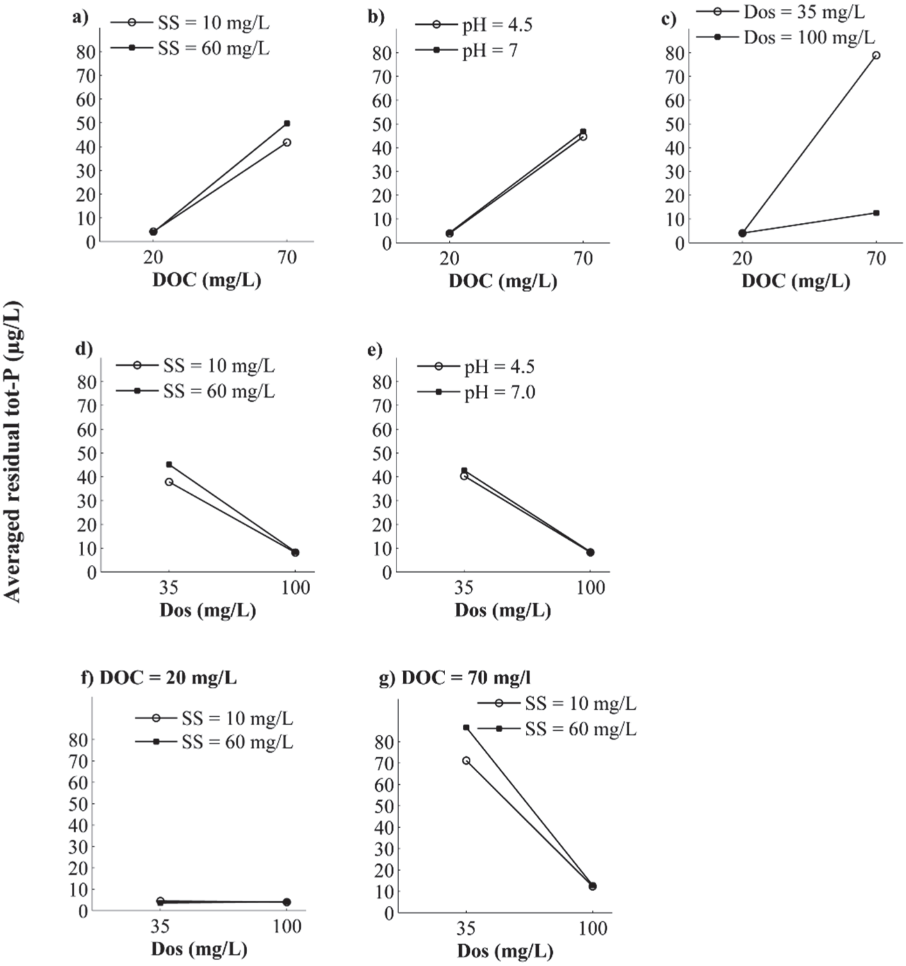


Fig. 23. The most significant factor interaction effects on the response variable residual total phosphorus (tot-P). Two-factor interaction effects (a–e) and three-factor interaction effects (f and g) (Paper IV; reprinted with permission from Elsevier).

5 Conclusions and suggestions for future research and treatment facility optimisation

Significant fluctuations in peat extraction runoff water quality are common and, together with issues related to process control and the design of chemical treatment facilities, contribute to the variations in water purification efficiency reported at commercial extraction sites. The laboratory studies conducted in this thesis work revealed that, among the inorganic and organic products tested, FS was the overall best performing coagulant. It achieved the best removal efficiencies, being particularly more effective in the removal of organic matter than the other products. However, this effective purification performance was obtained under optimum conditions. For these results to be replicated under field or real conditions, improvements to purification systems, including e.g. adjusting coagulant dosage according to water quality, introduction of slow mixing and provision of adequate retention time are needed.

Conclusions and suggestions for future research

A comparison of the observed advantages and disadvantages of all coagulants tested is presented in Table 11. In general, the data support the following conclusions and suggestions:

- Lower performance and higher dosage requirement were generally observed for solid metal salts than for products pre-dissolved prior to addition. The detrimental effects of low temperature, inadequate mixing and fluctuations in water pH were also significantly more evident in the purification levels achieved by solid coagulants.
- Although FS was the best performing coagulant, the synthetic and natural organic coagulants tested achieved satisfactory purification levels. Further investigations are required to determine the influence of factors such as mixing on the performance of organic polymers. Evaluation of products with varying MW and CD is suggested. Investigation of coagulant performance in terms of purification of particulate-rich humic samples is also recommended.
- Mixing during the flocculation stage had a more significant influence on purification by metal salt coagulants than mixing during coagulation;

Table 11. Summary of observed advantages and disadvantages of the coagulants tested.

Coagulant	Advantages	Disadvantages
Ferric sulphate (FS)	Best overall coagulant tested. High organic matter and phosphorus removal Good flocs with excellent settling characteristics	High residual iron and sulphate concentrations Significant effect on water pH (treated samples pH 3–4)
Aluminium sulphate (Alum)	Good overall purification efficiency Good flocs with good settling characteristics	Lower organic matter removal than FS (20–40%) Significant effect on water pH (treated samples pH 4–5) High residual aluminium concentration Higher dosage than FS (15–50%) Lower purification efficiency than FS at acidic pH conditions
PolyDADMAC (pDMAC)	Good overall purification efficiency Lower dosage than FS (55–80%) No effect on water pH	Low organic matter removal than FS (20–40%) Poor sedimentation characteristics at neutral pH for low turbidity water Toxicity
Polyamine (pAmine)	Satisfactory overall purification efficiency Lower dosage than FS (60%) No effect on water pH	Lower organic matter removal than FS (50%) Higher dosage than pDMAC (55%) High total nitrogen residual concentration
Tannin (Tan2)	Satisfactory overall purification efficiency Good flocs with excellent settling characteristics Small effect on water pH	Lower organic matter removal than FS (25%) Higher dosage than FS (55–200%) High total nitrogen residual concentration
Chitosan (Chit)	Satisfactory overall purification efficiency Good flocs with good settling characteristics Lower dosage than FS (40%) Small effect on water pH	Test product was not water soluble Lower organic matter removal than FS (30%) due to residual acetic acid dissolution

- Due to characteristics of the water samples tested (i.e. humic, low alkalinity, relatively low turbidity etc.), lower dosages were required for satisfactory purification in the treatment of samples with lower initial pH.
- Low water temperature (2–5 °C) had an overall negative effect on purification efficiency, especially on the removal of SS (<25%). All coagulants required between 50 and 200% longer settling times to reach 80% removal of turbidity at low water temperature.
- The higher molecular weight DOC fractions (biopolymers and humic substances) were more efficiently removed by all coagulants, with FS being the most efficient. Good removal rates were achieved by Tan2 (lowest CD polymer), indicating that charge neutralisation should not be considered as the only effective mechanism of HS removal. Further investigations to evaluate the influence of organic coagulant properties such as molecular weight and charge distribution on the removal of DOC fractions are suggested.
- The initial DOC concentration of the raw water samples and its interactions with coagulant dosage exerted the most significant influence on the purification efficiency achieved by FS. Thus, coagulant dosage should be adjusted according to variations in DOC concentration to ensure an efficient purification process where other pollutants of concern, such as SS, tot-P etc., are also efficiently removed.

Recommendations for optimisation of treatment facilities

- Cost/benefit evaluation of on-site pre-dissolution of solid coagulant is suggested.
- Coagulant dosage (FS) should not be kept constant, but adjusted according to variations in DOC concentration. Site-specific monitoring can be used to estimate organic matter concentration in different periods and pre-adjust the dosage accordingly. More effective dosage optimisation measures could result from continuous monitoring of organic matter concentration via on-line measurements of DOC or indicators such as UV254 absorption, and correlating this to automated adjustment of coagulant dosage.
- Preferential flow, leading to a decrease in retention time and poor purification results, was observed in the sedimentation basin studied. This appeared to be the result of inlet characteristics, thus inlet design for sedimentation basins should be carefully revised.

- Introduction of a slow mixing stage within or prior to the sedimentation basin is recommended to improve floc aggregation and the subsequent sedimentation process.
- Complete cost/benefit evaluation regarding the use of metal salts and organic coagulants is recommended. In addition to the cost of product used, this should include e.g. the costs of product transport, possible pH adjustment of purified water, equipment and energy used, sludge handling etc.
- The impact of temperature on the chemical purification process must be taken into consideration during the design or optimisation of treatment facilities. Longer sedimentation times should be allowed in sedimentation basins to ensure satisfactory SS retention.
- pH adjustments, when necessary, should be conducted at the outflow of chemical purification (prior discharge). This should lead to lower coagulant consumption.

Overall, due to its capability for removing nutrients, organic matter and SS, chemical purification has the potential to be an effective method to reduce pollutant loads not only from peat extraction, but also from land use activities such as agriculture and forestry. It could become an appropriate method for application in areas with sensitive ecosystems where high removal rates are required. The use of bio-coagulants can also improve the possibilities of nutrient recovery by recycling the sludge obtained on-site to e.g. agriculture as a soil amendment. However, an adequate level of process control is needed for effective results to be obtained and to ensure low variability and satisfactory purification levels.

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