Terhi Suopajärvi

FUNCTIONALIZED NANOCCELLULOSES IN WASTEWATER TREATMENT APPLICATIONS
TERHI SUOPAJÄRVI

FUNCTIONALIZED NANOCHELLOSES IN WASTEWATER TREATMENT APPLICATIONS

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Abstract

The chemicals currently used for wastewater treatment are mainly based on synthetic inorganic or organic compounds. Oil-derived polyelectrolytes are used for the removal of colloidal solids from wastewater by flocculation and coagulation, for example, while activated carbon adsorbents are typically used to remove soluble impurities such as heavy metals and recalcitrance organic matter. Many of these chemicals have associated negative health impacts, and use of activated carbon has proved to be expensive. Moreover, the present synthetic chemicals are not readily biodegradable or renewable. Thus there is a high demand for “green” water chemicals which could offer a sustainable solution for achieving high-performance, cheap water purification.

Water chemicals of a new type based on nano-scale particles (nanofibrils) derived from cellulose, i.e. nanocelluloses, are examined as possible bio-based chemicals for wastewater treatment. Two anionic nanocelluloses (dicarboxylic acid, DCC, and sulphonated ADAC) were tested as flocculants in the coagulation-flocculation treatment of municipal wastewater, while the flocculation performance of cationic nanocellulose (CDAC) was studied with model kaolin clay suspensions, and nanocelluloses produced from sulphonated wheat straw pulp fines (WADAC) were tested for the adsorption of lead (Pb(II)).

The anionic nanocelluloses (DCC and ADAC) showed good performance in treating municipal wastewater in a combined coagulation-flocculation process with a ferric coagulant. In the case of both anionic nanocelluloses the combined treatment resulted in a lower residual turbidity and COD in a settled suspension with highly reduced total chemical consumption relative to coagulation with ferric sulphite alone. Likewise, the CDACs resulted in powerful aggregation of kaolin colloids and maintained effective flocculation performance over wide pH and temperature ranges. The capacity of the nanofibrillated and sulphonated fines celluloses (WADAC) for the adsorption of Pb(II) was 1.2 mmol/g at pH 5, which is comparable to the capacities of commercial adsorbents.

Keywords: bioflocculants, biosorption, coagulation, dialdehyde cellulose, floc breakage, floc morphology, nanocellulose, nanofibril cellulose, wastewater
Suopajärvi, Terhi, Funktionalisoidut nanoselluloosat jättevesien käsittelyssä.
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Tiivistelmä

Jättevesien kemiallinen käsittely pohjautuu pääsääntöisesti synteettisten epäorganisteiden ja organisteiden kemikaalien käyttöön. Öljypohjaisia polyelektrolyittejä käytetään kolloidisten partikkeleen poistamiseen koaguloimalla ja flokkuloimalla, kun taas liuenteita epäpuhtauksia, kuten raskasmetalleja, poistetaan useimmiten adsorboimalla ne aktiivihiileen. Synteettiset vesikemikaalit valmistetaan uusiutumattomista luonnnonvaroista ja niiden hajoaminen luonnossa voi olla hidasta, minkä lisäksi monet näistä käytetystä synteettisistä vesikemikaaleista ovat terveydelle haitallisia. Aktiivihiilen käyttö puolestaan on kallista, johtuen sen korkeista valmistus- ja käyttökustannuksista. Uusille "vihreille vesikemikaaleille, jotka tarjoavat ympäristöystävällisempää, halpoja sekä tehokkaita ratkaisuja vedenpuhdistukseen, onkin suuri kysyntä.

Tässä työssä selluloosasta valmistettuja nanokokoisia partikkeleita, eli nanoselluloosia, on tutkittu yhtenä varteenotettavana biovaihtoehtona uusiksi kemikaaleiksi jättevesien puhdistukseen. Kahden anionisen nanoselluloosan (dikarboksyyli, DCC, ja sulfonoitu, ADAC) flokkauskykyä testattiin koagulointi-flokkulointi reaktioissa kunnallisen jätteveden puhdistuksessa. Kationisen nanosellun (CDAC) flokkauskykyä tutkittiin puolestaan kaoliinin aven malliliuoksilla ja vehnän korsiselun hienoaineista nanofibrilloimalla sekä sulfonoimalla valmistetuilla (WADAC) nanoselluloosamateriaaleilla testattiin lyijyn (Pb(II)) adsorptiota vesiliuoksiasta.


Asiakas: bioflokkuantti, biosorptio, dialdehydiselluloosa, flokin hajoaminen, flokin morfologia, jättevesi, koagulaatio, nanofibrilloselluloosa, nanoselluloosa
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Oulu, February 2015

Terhi Suopajärvi
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADAC</td>
<td>Sulphonated nanocellulose from kraft pulp</td>
</tr>
<tr>
<td>AGU</td>
<td>Anhydroglucose unit</td>
</tr>
<tr>
<td>CD</td>
<td>Charge density</td>
</tr>
<tr>
<td>CDAC</td>
<td>Cationic nanocellulose</td>
</tr>
<tr>
<td>CPAM</td>
<td>Cationic polyacrylamide</td>
</tr>
<tr>
<td>DAC</td>
<td>Dialdehyde cellulose</td>
</tr>
<tr>
<td>DCC</td>
<td>Dicarboxyl acid nanocellulose</td>
</tr>
<tr>
<td>FF</td>
<td>Form factor</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NFC</td>
<td>Nanocellulose from wheat pulp fines</td>
</tr>
<tr>
<td>PAC</td>
<td>Polyaluminium chloride</td>
</tr>
<tr>
<td>PACS</td>
<td>Polyaluminium chlorosulphate</td>
</tr>
<tr>
<td>PAM</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>PAS</td>
<td>Polyaluminium sulphate</td>
</tr>
<tr>
<td>PES-Na</td>
<td>Sodium polyethenesulphonate</td>
</tr>
<tr>
<td>Poly DADMAC</td>
<td>Poly(diallyldimethylammonium)chloride</td>
</tr>
<tr>
<td>RO</td>
<td>Roundness</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethyl-1-piperidinyloxy</td>
</tr>
<tr>
<td>WADAC</td>
<td>Sulphonated nanocellulose from wheat pulp fines</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
</tr>
<tr>
<td>$b$</td>
<td>Constant related to the affinity of the adsorbent for binding sites</td>
</tr>
<tr>
<td>$C_e$</td>
<td>Equilibrium metal concentrations</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Initial metal concentrations</td>
</tr>
<tr>
<td>$K_F$</td>
<td>Freundlich constant, relative adsorption capacity</td>
</tr>
<tr>
<td>$n$</td>
<td>Freundlich constant, measure of the nature and strength of the sorption process and the distribution of active sites</td>
</tr>
<tr>
<td>$Q^0$</td>
<td>Langmuir constant, representing monolayer sorption capacity</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Adsorbed metal ions on the adsorbent</td>
</tr>
<tr>
<td>$R_{br}$</td>
<td>Rate of aggregate breakage</td>
</tr>
<tr>
<td>$R_{col}$</td>
<td>Rate of particle collision (frequency of collision)</td>
</tr>
<tr>
<td>$R_{floc}$</td>
<td>Floc growth rate</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Collision efficiency factor (fraction of the collisions resulting in attachment)</td>
</tr>
</tbody>
</table>
List of original publications

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


The author of this thesis was the primary author of papers I, II and IV and co-author of paper III. The author’s responsibilities included the experimental design, data analysis and reporting of the results in papers I, II and IV, and participation in the data analysis and writing of the paper in paper III. The co-authors participated in the experimental design, analysis and writing of the publications.
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1 Introduction

1.1 Background

Rapid industrialization and modern agricultural and domestic activities have greatly increased the demand for fresh water, and in turn have generated large amounts of wastewater containing a number of pollutants that are harmful to living organisms (Gupta et al. 2009). The total of about 71,000 municipal wastewater treatment plants (WWTPs) operating in the area of the EU, including Iceland, Norway and Switzerland (Recycling Portal EU 2014) produced approximately 10 million tons (dry matter) of sewage sludge annually during the years 2003-2006, since when amount has been continually increasing (Wei et al. 2003, Milieu Ltd et al. 2010). Wastewater and wastewater sludges contain nutrients (phosphorous and nitrogen compounds) and potentially toxic elements including heavy metals, all arising from domestic sources (i.e. plumbing, body care products, etc.), surface run-off and/or commercial and industrial activities (Milieu Ltd et al. 2010). Since polymers such as polyacrylamides are extensively used as flocculation aids in wastewater treatment and to enhance the mechanical dewatering of sludge, synthetic polymers may constitute up to 1% of the amount of dry sludge (Milieu Ltd et al. 2010).

Wastewater contains both soluble compounds and small solid colloidal material ranging in particle size from 0.001 to 10 µm. Colloidal particles increase the turbidity, colour and COD (chemical oxygen demand) of the water (Bratby 2006) and have a tendency to adsorb various ions from the surrounding medium which impart an electrostatic charge to the colloids relative to the bulk of the surrounding water in addition to dissociation (Wang et al. 2005, Bratby 2006). The small size of colloidal particles (<1 µm) implies that sedimentation rates are very slow compared to diffusion and thus a colloid remains stable as long as repulsive interactions between the particles prevent aggregation due to collisions (Wang et al. 2005). Thus colloids must be gathered together into larger aggregates in order to remove them and reduce the turbidity of municipal and industrial wastewater (Wang et al. 2005, Song et al. 2010). In coagulation, such aggregates can be produced using inorganic aluminium or iron-based metal salts or synthetic short-chain polymers as coagulants. Alternatively, flocculation can be used to produce larger aggregates using high-molecular-weight polymers. In many cases combined coagulation-flocculation treatments are applied in order to achieve the most cost-
effective treatment efficiency. Combined treatment can reduce the coagulant doses required, the volume of sludge and the ionic load of the wastewater (especially the level of aluminium), and thereby save in overall costs (Bolto & Gregory 2007).

The chemicals typically used for flocculation are macromolecular, water-soluble polymers such as synthetic polyacrylamides, polyacrylic acids and polystyrene sulphonlic acids and their derivatives, which are not readily biodegradable (Chakrabarti et al. 2008, Brostow et al. 2009). Synthetic polymers are efficient for producing large-branched flocs (Singh et al. 2000), but these flocs typically have a low shear resistance and can easily be broken down, causing the release of organic compounds and an increase the quantity of fine particles in the purified water (Brostow et al. 2009, Zhou et al. 2014). Moreover, these polymers may also contain unpolymerized monomers and additives that can be neurotoxic and/or carcinogenic (Rudén 2004, Ho et al. 2010). In addition, synthetic polymers are typically produced from oil-based raw materials, which means that they are non-renewable. Consequently, there has been a growing interest in replacing oil-based flocculants with more sustainable natural bio-based alternatives, which also produce more shear-resistant flocs.

There has also been an expansion in industrial activities that produce wastewater containing many soluble compounds like, recalcitrance organic pollutants and heavy metals. Especially, the contamination of water with heavy metals is a serious cause of environmental and human health problems (Doan et al. 2008, Wan Ngah & Hanafiah 2008, Duan et al. 2013). Unlike organic waste, heavy metals are non-biodegradable and can accumulate in living tissues, causing various diseases and disorders, since they can be toxic and/or carcinogenic (Wan Ngah & Hanafiah 2008, Fu & Wang 2011). The heavy metals that are most commonly associated with pollution and toxicity problems include zinc (Zn), copper (Cu), nickel (Ni), mercury (Hg), cadmium (Cd), lead (Pb) and chromium (Cr) (O’Connell et al. 2008, Fu & Wang 2011).

Heavy metals can be removed from effluents using chemical reduction, electrochemical treatment, ion exchange, precipitation with hydroxides, carbonates and sulphides (Garg et al. 2008), evaporative recovery or adsorption onto activated carbon, for instance (Min et al. 2004, O’Connell et al. 2008, Gupta & Babu 2009). These methods are expensive and inefficient in many cases, however, especially when the metal concentration is low (<100 ppm) (Guzel et al. 2008, O’Connell et al. 2008, Gupta & Babu 2009). The sludge generated in the precipitation method also poses challenges in connection with its handling, treatment and disposal by landfilling, while ion exchange requires high capital and operational costs due to
the chemicals used for the regeneration of resins (Doan et al. 2008, O’Connell et al. 2008). Electrolysis is an advantageous method if the concentration of metals is high, but it is inefficient at low metal concentrations (Doan et al. 2008, O’Connell et al. 2008).

Of all the treatments, adsorption is one of the most feasible and effective for removing heavy metals from wastewater. Activated carbon adsorbents are typically used for this purpose, but the high material costs are restrictive in many cases (O’Connell et al. 2008). Consequently, low-cost sorbents derived from abundant renewable resources, industrial by-products or waste materials have been considered as attractive alternatives for heavy metal removal (Babel & Kurniawan 2003, Crini 2005, Sud et al. 2008, Gupta & Babu 2009). Cellulosic waste materials such as sugarcane bagasse (Karnitz Jr et al. 2007), cotton linters (Nada et al. 2002) and wheat straw (Chojnacka 2006, Doan et al. 2008), have already been investigated for the adsorption Cd(II), Cu(II), Mn(II), Mg(II), Sr(II) and Pb(II) ions, for example, but more development work with regard to the adsorption performance and the regeneration of these biosorbents is still needed for them to be viable options in commercial applications.

The rapid progress made in the nanosciences, especially with nanocelluloses, offer a potential new type of material for use in water treatment in the form of nanoparticles. Nanocelluloses, for example, with a high aspect ratio and surface area combined with a flexible structure, may produce stronger flocs that will resist shearing in flows and result in improved purification efficiency. Furthermore, when targeting water-soluble flocculants, the typical problem has been a decrease in the molecular weight of the molecules, which can be avoided when using nanocelluloses of micrometre length. Anionic cellulose (ADAC) in the form of nanoparticles (Liimatainen et al. 2012a) has recently been found to result in better flocculation performance than the corresponding fully water-soluble derivatives (Liimatainen et al. 2012a). Nevertheless, the use of nanocellulose materials in wastewater treatment applications has not been widely investigated as yet. This work focuses on functionalized nanocelluloses as potential new chemicals for the removal of solids from aqueous solutions by coagulation-flocculation treatment and metal adsorption.

1.2 Wastewater treatment

There are number of treatment processes available for the removal of solids and soluble impurities from wastewater. These can be categorized into physical,
chemical or biological treatments, and include processes such as sedimentation, precipitation, extraction, evaporation, coagulation-flocculation, flotation, electrocoagulation, filtration, adsorption, ion exchange, bio-degradation and electrochemical treatment (Harif et al. 2012, Das et al. 2013, Sher et al. 2013). The efficient treatment of wastewater usually requires a number of steps, and it is often appropriate to combine more than one method (Sher et al. 2013). Coagulation and flocculation are amongst the most widely practised technologies for removing solids from industrial and municipal wastewater, while adsorption is the method most frequently used metals in dilute solutions (Gadd 2009, Fu & Wang 2011).

1.2.1 Coagulation and flocculation

Coagulation and flocculation are simple, cheap, effective and the most traditional ways to treat wastewaters (Song et al. 2010, Wang et al. 2011). Coagulation is a process in which the colloids or particles in a suspension are destabilized, causing the formation of small aggregates of particles (Jarvis et al. 2005, Bratby 2006, Tripathy & De 2006), while in flocculation the resulting destabilized and aggregated particles or other colloidal and particular materials are gathered into larger aggregates (Jarvis et al. 2005, Bratby 2006). Flocculation treatment can also be used on its own to produce larger generally porous and loosely assembled aggregates called flocs.

Colloids and their stability

The stability of suspension depends on the surface properties of the colloids which are divided into two general classes: lyophobic and lyophilic or in water treatments hydrophobic and hydrophilic (Everett 1988, Wang et al. 2004). Colloids possess a very high ratio of surface area to mass (Everett 1988, Bratby 2006, Singh et al. 2009) and hydrophilic colloids interact with water and thus, are more demanding to aggregate than hydrophobic colloids (Wang et al. 2004). The strength of the colloids charge depends on the quality of colloids and the pH, the temperature and the ionic strength of the solvent (Everett 1988). In most cases colloidal particles acquire a negative primary charge in an aqueous environment, which creates repulsive forces that keep the particles apart and prevent their agglomeration (Wang et al. 2005; Bratby 2006). The surface charges of colloids influence the distribution of the nearby ions in a liquid, so that counter-ions accumulate on the surfaces of the suspended particles, with a higher concentration of counter-ions close to the
surface than in the bulk of the liquid. This concentration falls off with increasing distance from the particle surface (Fig. 1) (Singh et al. 2009). Thermal motion (Brownian movement) and ionic repulsion or attraction lead to the formation of an electrical double layer made up of a charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the nearby liquid (Everett 1988, Bratby 2006) (Fig.1). The total potential at the surface of a primary charged particle is called the Nernst potential (Wang et al. 2005, Bratby 2006, Singh et al. 2009). The dense layer of counter-ions fixed the surface of the primary particle is called the Stern layer and after this layer exists a more diffused layer. Only the bound layer moves with the particle. There is a shear plane between the bound layer and the diffuse layer, so that the difference in potential between the shear plane and the bulk solution, known as the zeta potential (Fig. 1), determines the potential at the surface of the particle (Everett 1988, Wang et al. 2004). As the zeta potential increases, the repulsion between particles with the same charge becomes stronger and the suspension more stable (Everett 1988, Singh et al. 2009).

All colloidal particles also possess forces of attraction due to van der Waals’ forces. They arise from; i) the electronegativity of some atoms is higher than for others in the same molecule, ii) vibration of charges within one atom creates a rapidly fluctuating dipole or iii) approaching particles induce vibrations in phase with each other, resulting in an attractive force between the two oppositely oriented dipoles (Everett 1988, Wang et al. 2004). The magnitude of the force varies inversely with distance between particles, increasing rapidly with decreasing distance. If particles come close enough for these forces to take over, they will adhere (Wang et al. 2005).
The aggregation of particles occurs due to destabilization of the colloid particles caused by the addition of a water-soluble coagulant or flocculant or by increasing the ionic strength (Everett 1988, Singh et al. 2009). In coagulation (Fig. 2) the suspended particles are usually electrically neutralized with iron or aluminium hydroxides, while in flocculation they are interlinked by means of molecular chains, for example (Singh et al. 2009).

When particles are adequately destabilized, they will aggregate on collision with other destabilized particles. These collisions can occur through Brownian diffusion and fluid motion (Everett 1988, Gregory 2009). The concentration of colloids has a large effect on the dosage required and the efficiency of coagulation (Zouboulis et al. 2008).

Besides the concentration of colloids and the amount of coagulant, the pH also has a considerable effect on the stabilization of colloidal suspensions, because the surface charge of the colloids and the predominance of a particular hydrolysis species of coagulant are largely dependent on pH (Brathy 2006). The isoelectric point, which varies with the ionic strength of the solution, is the pH value at which the surface charge of the colloids is neutralized (Everett 1988, Wang et al. 2004).
The presence of H⁺ or OH⁻ ions in the potential-determining layer may cause a particle charge to be more positive or less negative at pH values below the isoelectric point and the reverse at high pH values above the isoelectric point (Wang et al. 2005).

**Coagulation and flocculation mechanisms**

When high concentrations of simple salts are introduced into a stabilized colloidal dispersion, the added counter-ions penetrate into the diffuse double layer, which makes the double layer compress and hence reduces the long-range repulsion between colloids enabling the aggregation by van der Waals forces (Everett 1988, Wang et al. 2004, American Water Works Association 2011). This effect is stronger the higher the charge of the counterions according the Schulze-Hardy rule. For example, the relative power of Al³⁺, Mg²⁺, and Na⁺ for the coagulation of negative colloids is shown to vary in the ratio of 1000:30:1(Everett 1988, Wang et al. 2004; American Water Works Association 2011).

Fig. 2 shows the main mechanisms of coagulation and flocculation. In charge neutralization a coagulant or flocculant with a high positive charge is adsorbed on to the surfaces of negatively charged colloids (Tripathy & De 2006, Singh et al. 2000, American Water Works Association 2011). The added chemicals penetrate into the diffuse double layers surrounding the particles rendering them denser and hence thinner and smaller in volume, which enables the particles to move closer to each other (Wang et al. 2005, Bratby 2006). When a metal salt coagulant is added to water at a concentration sufficiently high to cause the precipitation of amorphous metal hydroxide (M(OH)₃), colloid particles can be enmeshed in these precipitates ( Li et al. 2006, Ersoy et al. 2009). This process is called sweep coagulation (Fig.2).

Bridging (Fig. 2) occurs when a segment of a polymer chain adsorbs to more than one particle, linking the particles together (Li et al. 2006; Bolto & Gregory 2007). One essential requirement for bridging is that there should be a sufficient unoccupied surface on a particle for the attachment of segments of polymer chains already adsorbed on other particles (Bolto & Gregory 2007). At a pH above the isoelectric point, the net charge of colloids is negative and the polymer chain conformation more extensive, which promotes this bridging flocculation mechanism (Yang et al. 2012, Das et al. 2013). In systems where the bridging mechanism predominates, an increase in the MW of the flocculant improves flocculation irrespective of the charge density (Ghimici & Nichifor 2010).
In patch flocculation (Fig. 2), a polymer or coagulant adsorbs onto an oppositely charged particle surface to give a non-uniform distribution of the surface charge (Yukselen & Gregory 2004, Bolto & Gregory 2007). If a polyelectrolyte has a high charge density it will adsorb to the particles in a flat configuration, leading to patches with localized excesses of polymer charge (Bouyer et al. 2001, Yukselen & Gregory 2004). Direct electrostatic attraction between oppositely charged patches promotes aggregation, and particles with a strong negative zeta potential, such as silica, will aggregate by patch mechanisms in response to polyelectrolytes with a high cationic charge density (>0.15), while a low cationic charge density (<0.15) will favour bridging (Tripathy & De 2006).

**Fig. 2. Mechanisms of coagulation and flocculation.**

**Coagulants and flocculants**

Coagulants are typically divalent or trivalent metallic salts or polymers that have a low solubility in the pH range used (Wang et al. 2005). Metal salts hydrolyze rapidly in wastewater to form cationic species which are adsorbed by negatively
charged dirt particles, resulting in simultaneous surface charge reduction (Snodgrass et al. 1984, Li et al. 2006). These cations can destabilize suspensions by charge neutralization, adsorption and bridging or by sweeping the colloidal or particular material from the suspension (Wang et al. 2005, Bratby 2006). There are also low molecular weight polyelectrolytes with a high charge density such as polyDADMAC (poly (diallyldimethylammonium chloride)) that are used as primary coagulants. The low resistance to oxidizing agents of polymers, their selectivity for certain types of particulate and their probable short storage life have nevertheless restricted their use as primary coagulants (Bratby 2006). Pre-polymerized coagulants such as PAC (polyaluminium chloride), PAS (polyaluminium sulphate) and PACS (polyaluminium chlorosulphate) have been the most widely used coagulants during recent decades since they are able to perform over a wide range of pH, temperature and colloid concentration as compared with conventional metal salts (Zouboulis & Tzoupanos 2009). However, use of inorganic coagulants, especially aluminium compounds, may have adverse effects on humans and the environment (Zouboulis et al. 2004, Song et al. 2010, Zhao et al. 2011).

Organic flocculants can be natural or synthetic polymers and they may be non-ionic, cationic or anionic, with a variable charge density (Brostow et al. 2009). Ionic polymers are often referred to as polyelectrolytes (Bolto & Gregory 2007). The synthetic polymers used in flocculation are typically water-soluble and their molecular weight (MW) can range from a few thousand to tens of millions (Bolto & Gregory 2007). Cationic polymers usually involve quaternary ammonium compounds and protonated amines such as functionalized poly-acrylamides (PAMs), usually Poly(Trimethyl(3-methacrylamidopropyl)ammonium) chloride (C-PAM), with varying degrees of substitution at the amide group, or poly(diallyldimethyl-ammonium chloride) (polyDADMAC) (Bolto & Gregory 2007, Chimamkpam et al. 2011). Extensively used anionic polyelectrolytes are PAMs functionalized with carboxylic acid and PAA (polyacrylic acid) with a low charge density. Synthetic non-ionic polymers such as PEO (Polyethylene oxide), PAM or PVA (polyvinyl alcohol) also often contain 1-3% of anionic groups (Bolto & Gregory 2007, Gregory & Barany 2011). Natural flocculants are presented in more detail in the next section (Chapter 1.4).

For effective flocculation, polymers need to be adsorbed to particles by electrostatic and/or hydrophobic attraction, hydrogen bonding and ion binding (Bolto & Gregory 2007, Ghimici & Nichifor 2012). These interactions lead to various conformations of the adsorbed polymer chains, such as trains, loops and
tails, which permit different floculation mechanisms (Bolto & Gregory 2007). It is quite common, however, for more than one mechanism to operate simultaneously, depending on the polymer size and shape, the solution and its particle properties (Ghimici & Nichifor 2012).

**Floc strength**

Floc strength is dependent upon the inter-particle bonds between the components of the aggregate (Jarvis *et al.* 2005, Li *et al.* 2006). The floc structure continuously changes during flocculation, because the internal bonds of the flocs break under shear forces and re-establish themselves at more favourable points (Yu *et al.* 2012). Particles may flocculate under low turbulence and break up when exposed to high turbulence (Mikkelsen & Keiding 2002). In any case floc growth is inhibited by such breakage, so that the rate of floc formation should be regarded as a as a matter of the balance between floc formation and floc breakage (Jarvis *et al.* 2005). After a characteristic time, a steady state is reached between aggregation and fragmentation at the chosen shear rate. In general, the overall floc growth rate ($R_{floc}$) can be defined as (Jarvis *et al.* 2005, Harif *et al.* 2012):

$$R_{floc} = \alpha R_{col} - R_{br},$$  \hspace{1cm} (1)

where ($R_{col}$) is the rate of particle collision (frequency of collisions), ($R_{br}$) the rate of aggregate breakage and $\alpha$ the collision efficiency factor (fraction of the collisions that result in attachment).

The floc structure, particle bond strength and number of individual bonds all affect the floc strength (Li *et al.* 2006). Densely packed aggregates have a high fractal dimension, while large, highly branched and loosely bound structures result in a lower fractal dimension (Li *et al.* 2006). Also the size and shape of the constituent particles of the flocs influence the floc strength and the efficiency of the separation processes (Yukselen & Gregory 2004, Li *et al.* 2006).

The break-up of flocs can occur by two mechanisms: fragmentation into smaller parts causes a shift towards a smaller average floc size with no change in the primary particle population (Mikkelsen 2001, Mikkelsen & Keiding 2002, Yuan & Farnood 2010), whereas erosion of primary particles from the floc surface causes a shift in the relative mass of the two particle size classes (Mikkelsen 2001, Mikkelsen & Keiding 2002). Thus erosion implies a pronounced increase in the primary particle population, whereas the relative change in floc size and mass may
be minor (Mikkelsen & Keiding 2002). Breakage of the flocs will result in the release of organic compounds, and an increase the quantity of fine particles greater variability in the distribution of broken particles, which may detract not only from the dewatering of the resulting sludge but also from the quality of treated wastewater (Zhou et al. 2014).

Depending of mechanism of flocculation, flocs may re-grow after breakage. Irreversible breakage suggests that chemical bonds are broken during floc disruption. When particle interaction is of a physical nature (such as van der Waals or electrostatic attraction) there is no obvious reason why aggregates should not re-form after breakage (Yukselen & Gregory 2004). Flocs formed by charge neutralization have total recoverability, while sweep flocs have poor re-growth after breakage (Yukselen & Gregory 2004, Yu et al. 2010a, Zhou et al. 2014). In the sweep coagulation the collision efficiency of broken flocs is reduced, as nearly the entire particle surface is covered by positively charged iron or aluminum hydroxides (Yu et al. 2010b). In the case of polymeric flocculants, high shear rates (especially under turbulent conditions) may cause scission of polymer chains and adsorbed polymer could adopt a more flat configuration during the breakage phase (Yukselen & Gregory 2004, Zhou et al. 2014). However, these considerations do not apply when charge neutralization or patch flocculation are responsible for flocculation, so that the re-growth of flocs can be expected in such cases (Yukselen & Gregory 2004).

### 1.2.2 Adsorption

Adsorption is known to be an effective and economic method for removing impurities from wastewater. Adsorption can be a reversible process, which implies possible regeneration of the adsorbents through suitable desorption processes (Fu & Wang 2011). Adsorption of a molecule or ion from a solution to the surface of an adsorbent involves three steps: 1) removal of the molecule from the solution, 2) removal of the solvent from the solid surface, and 3) attachment of the molecule to the surface of the solid (Crini 2005, Bratby 2006).

Either a hard or a soft classification can be used to predict how different functional groups will bind particular metal cations (Fig. 3). According to these classifications, acids and bases have an attractive interaction and the most stable interactions are hard acid-hard base and soft acid-soft base ones. Hard acids preferentially bind to ligands containing oxygen, while soft acids preferentially bind to ones containing S and N (Gadd 2009, Hubbe et al. 2011). The hard/soft
scheme (Fig. 3) predicts that bonds formed between hard acids and hard ligands will be predominantly ionic, whereas soft acid-ligand complexes are more covalent in character (Gadd 2009). These definitions are not absolute, and variations may cause by metal concentrations, for example, or by the relative metal concentrations in mixtures where competitive effects may occur (Gadd 2009).

![Figure 3: The hard/soft classification of acids and bases.](image)

Adsorption mechanisms are dependent on the degree of adsorbate-adsorbent interaction and the adsorbate-solvent interactions (Ho et al. 2000). Adsorption processes may include physical and chemical adsorption like, ion exchange and chemical complexation (Ho et al. 2000, O'Connell et al. 2008). It is also possible for more than one of these mechanisms to be present and affect the adsorption interaction (Crini 2005, O'Connell et al. 2008, Gadd 2009). In the case of the uptake of metals by bio-based sorbents, ion exchange and chemical complexation, as shown in Fig. 3, are the most common mechanisms (Doan et al. 2008, Gupta et al. 2009).

Ion exchange is the mechanism by which adsorbing metal ions take the place of other species already associated with the sorbent surface (Fig. 4). Thus it is the replacement of an adsorbed, readily exchangeable ion by another (Gadd 2009). These entities may be ions such as Na⁺, Ca²⁺ or proton H⁺ (Dąbrowski et al. 2004, Hubbe et al. 2011). Higher affinity for exchanged ion will lead to desorption of an associated ion from surface sites and uptake of an exchanged ion (Hubbe et al. 2011).
Ion exchange is mainly concerned with the stoichiometry of the displacement of bound ions by dissolved ions (Hubbe et al. 2011).

In chemical complexation, the functional groups of the adsorbent surface have site-specific interactions with particular kinds of metal ions (Sud et al. 2008, Hubbe et al. 2011) (Fig. 4). A molecule or ion can be held on the solid surface by ionic, covalent, hydrogen or dipolar bonding, i.e. processes of chemical adsorption (Bratby 2006), while adsorption processes arising from van der Waals attraction are referred to as physical adsorption (Bratby 2006). In chemical complexation the ability of a surface site to bind various metals is attributed to the radius of the metal ion and the symmetry of its valence electron orbitals relative to the positions of the surface-bound atoms at the site of adsorption (Hubbe et al. 2011).

![Fig. 4. Illustration of the ion exchange (left) and chemical complexation (right).](image)

The removal of metal ions from aqueous solutions by adsorption depends on the solution’s pH, the degree of ionization of the different species and the surface characteristics of the adsorbent (Karnitz Jr et al. 2009). Thus the pH can influence the protonation of the functional groups on the adsorbent as well as the solution chemistry of the metal ions (Liu et al. 2010).

Predicting the rate at which adsorption takes place for a given system is an important part of adsorption system design (Sud et al. 2008). Numerous kinetic models are available, such as first-order and second-order reversible ones and first-order and second-order irreversible ones, and also pseudo-first-order and pseudo-second-order ones, to describe the reaction order of adsorption systems based on the concentration of the solution (Sud et al. 2008, Gadd 2009, Hubbe et al. 2011). The adsorption process is often characterized using a number of isotherm models. These isotherms represent the relationship between the amount adsorbed per unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium (Sud et al. 2008). These include the most common Langmuir (1918) and Freundlich (1926) isotherms and other related models (Altin et al. 1998,
O’Connell et al. 2008, Hubbe et al. 2011). The Langmuir and Freundlich models are widely used, since they are simple and are able to describe the experimental results over a wide range of concentrations (Altin et al. 1998, Perić et al. 2004). They have also been found to fit best with most of the biosorbents, including cellulosic adsorbents (O’Connell et al. 2008, Hubbe et al. 2011, Hubbe et al. 2012). Mathematical correlation of the Langmuir isotherm has provided a basis for developing other models, which include the similarity between adsorption and ion exchange, Gaussian energy distribution, degree of surface heterogeneity and the range of high solute concentrations (Perić et al. 2004, O’Connell et al. 2008). The most commonly used Langmuir isotherm defines the equilibrium parameters of homogenous surfaces, monolayer adsorption and the distribution of adsorption sites (Perić et al. 2004, O’Connell et al. 2008, Hubbe et al. 2011).

The Freundlich isotherm is the earliest known relationship describing non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption with a non-uniform distribution of adsorption heat and affinities over a heterogeneous surface. The amount adsorbed is the sum of the adsorption at all sites (each having bond energy), with the stronger binding sites are occupied first and the adsorption energy exponentially decreasing upon completion of adsorption process (Gadd 2009, Foo & Hameed 2010, Hubbe et al. 2011).

1.3 Natural polymers in wastewater treatment

In view of the increased demand for “green” and sustainable water treatment technologies, natural polymers have been widely investigated as means of replacing synthetic and inorganic water chemicals (Song et al. 2010). Biodegradability is one of the most important environmental aspects of water chemicals, as it will affect their long-term ecological impact (Xing et al. 2010). On the other hand, biochemicals derived from cheap, unwanted by-product possessing high performance, e.g. high selective adsorption capacity, are to be preferred (Wan Ngah & Hanafiah 2008, Dang et al. 2009). In recent years it has been polysaccharides such as guar gum (Banerjee et al. 2013), starch (Abdel-Aal et al. 2006, Xing et al. 2010), chitosan (Lu et al. 2011, Yang et al. 2011), cellulose (Song et al. 2010) and their derivatives such as dextran (Ghimici et al. 2009, Ghimici & Nichifor 2010 and pullulan (Ghimici et al. 2010, Constantin et al. 2013) that have particularly attracted attention as flocculation and adsorption aids (Zhang et al. 2013).
Aqueous polysaccharide materials possess a very high swelling capacity on account of the hydrophilic nature of the repeating polysaccharide units. Consequently, polysaccharide networks expand sufficiently during adsorption to permit the fast diffusion of pollutants. Even though neutral cross-linked polysaccharides have good adsorption capacity, this can be further improved by grafting various functional groups onto the polymer network or backbone (Constantin et al. 2013). High solubility, which is a typical requirement for synthetic polymers such as flocculation agents, is not necessary in the case of polysaccharide chemicals (Liimatainen et al. 2012a, Lekniute et al. 2013), so that cationic starch particles, for example, have been reported to exhibit more than twice the flocculation efficiency of soluble cationic starches (Klimaviciute et al. 2010) while anionic particulate nanocellulose flocculants have proved more effective in the coagulation-flocculation of kaolin clay than soluble ones (Liimatainen et al. 2012a).

The most widely used natural flocculants are starch and its derivatives (Tripathy & De 2006). There are various sources of starches, including potatoes, corn, cassava (manioc), arrowroot and yams (Bratby 2006). Starches are highly polymerized carbohydrates which can be non-ionic, cationic or anionic depending on the form of processing and the substitutions made (Bratby 2006). Cationic starches, which are the most commonly used, have a medium MW (10^5 – 10^6 gmol⁻¹) and their CD can be low or medium (Bolto & Gregory 2007). Cationic starches with a low degree of substitution in particular have been used for flocculation purposes in papermaking (Lekniute et al. 2013). Their main disadvantage, however, is a very narrow concentration range for efficient phase separation, so that a small overdose can restabilize the system (Lekniute et al. 2013). Thus flocculation with soluble and high-cationized starch mostly follows the charge neutralization mechanism. At a higher than optimal dose starch macromolecules cover most of available anionic sites on each particle and may impart an positive electric charge to them which is high enough to cause mutual repulsion (Sableviciene et al. 2005).

Chitosan is derived from the deacetylation of chitin, which is the most abundant aminopolysaccharide in nature and has been found to complex pollutants such as metals to a pronounced degree (Gadd 2009, Lu et al. 2011, Elsabee et al. 2012). The industrial production of chitosan is nevertheless limited by harmful effluents, as it generates large quantities of concentrated alkalines and degradation products. In addition, conversion to chitosan at high temperature with a strong alkali can cause variabilities in the properties of the product and increase production costs (Gadd 2009). Chitosan has a low molecular weight and poor
solubility in water under neutral or alkaline conditions, factors which limit its feasibility for flocculation applications (Wang et al. 2009, Lu et al. 2011, Yang et al. 2011). On the other hand, it has been found to be a good adsorbent for many heavy metals, mainly on account of its hydrophilicity, due to the large numbers of hydroxyl groups and high-activity primary amino groups and the flexible structure of its polymer chain (Babel & Kurniawan 2003).

Cellulose is the most abundant renewable biopolymer on the Earth (Saito & Isogai 2005). Natural cellulose fibres are prevalent throughout the world in plants such as grasses and reeds and in the stalks and woody parts of the vegetation in general (Azizi Samir et al. 2005). The worldwide production of cellulosics is estimated to be between $10^{10}-10^{11}$ tons each year (Azizi Samir et al. 2005, Habibi et al. 2010, Lavoine et al. 2012, Abdul Khalil et al. 2014), and with only about $6 \times 10^9$ tons of this processed the paper, corrugating, chemical and textile industries (Simon et al. 1998, Lavoine et al. 2012).

In general, cellulose is a strong, fibrous, water-insoluble substance that plays an essential role in maintaining the structure of plant cell walls (Habibi et al. 2010). The properties of cellulosic fibres are greatly influenced by factors such as their chemical composition, internal fibre structure, microfibril angle, cell dimensions and defects, which vary between plant species and between parts of the same plant (Siqueira et al. 2010). Regardless of its source, cellulose can be characterized as a high-molecular-weight linear homopolysaccharide of $\beta$-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed 180° with respect to its neighbours (Habibi et al. 2010, Siqueira et al. 2010) (Fig. 5). The repeating segment is frequently taken to be a dimer of glucose known as cellobiose (Habibi et al. 2010, Siqueira et al. 2010) (Fig. 5), while the monomer, named the anhydroglucose unit (AGU), bears three hydroxyl groups (Fig. 5), which confer upon cellulose its most important properties, its multi-scale microfibrillated structure, its hierarchical organization, of crystalline versus amorphous regions and its highly cohesive character (Lavoine et al. 2012). In nature, cellulose chains have a DP of approximately 10 000 anhydroglucopyranose units in wood and 15 000 units in cotton (Azizi Samir et al. 2005, Siqueira et al. 2010).
There are four polymorphs of cellulose (cellulose I-IV). Native cellulose consists of cellulose I with two slightly different crystalline structures, cellulose I\(\alpha\) and cellulose I\(\beta\) (Azizi Samir et al. 2005, Habibi et al. 2010, Siqueira et al. 2010), and this can be further converted to cellulose II-IV by chemical and mechanical treatments (Azizi Samir et al. 2005, Siqueira et al. 2010, Lavoine et al. 2012).

Various cellulosic raw materials such as kapok (Duan et al. 2013), sugarcane bagasse (Gurgel et al. 2008, Karnitz Jr et al. 2009), corncobs (Vaughan et al. 2001), cotton linters (Nada et al. 2009, Dong et al. 2013) and wheat straw (Chojnacka 2006) have been examined as possible water treatment chemicals, but native cellulose has a relatively low reactivity towards adsorption or flocculation (Rudie et al. 2006, Nikiforova & Kozlov 2011). Thus the introduction of new functional groups on the surface of cellulose can increase its surface polarity and hydrophilicity, which can in turn enhance the adsorption of polar adsorbents and the selectivity of the cellulose for the target pollutant (Constantin et al. 2013).

**1.3.1 Nanocelluloses**

Nanocelluloses, elemental nano-sized constituents of plant fibres (Fig. 6), have acquired an extra reputation relative to conventional cellulose fibres due to their huge surface area, high aspect ratio and high Young’s modulus of 145 GPa (Iwamoto et al. 2009) resulting from high crystallinity (Klemm et al. 2011, Abdul Khalil et al. 2014, Jin et al. 2014). Furthermore, being as nature materials, nanocelluloses are biodegradable, biocompatible and renewable (Jin et al. 2014).

The lateral size of cellulose molecule chains is about 0.3 nm, and these chains form bundles of elongated fibrils still with nano-scale diameters. The cellulose chains are stabilized laterally by hydrogen bonds between their hydroxyl groups (Zimmermann et al. 2004) (Fig. 6).
There are three main categories of nanocelluloses (Klemm et al. 2011); nanofibrillated celluloses, nanocrystalline celluloses and bacterial celluloses. Nanofibrillated celluloses are elongated strains of superfine fibrils, while nanocrystalline celluloses are rod-like particulates consisting of crystalline cellulose (Zimmermann et al. 2004, Siqueira et al. 2010, Abdul Khalil et al. 2014). Bacterial cellulose is produced by down-to-top synthesis, where specific bacteria synthetize bundles of cellulose nanofibrils from low molecular sugars and alcohols (Klemm et al. 2011). The focus in this thesis will be on the nanofibrillated celluloses.

Nanofibrillated celluloses exhibit both amorphous and crystalline parts (60%-80%) in their flexible fibrillar strands, which have typical lateral dimensions of 2-80 nm and are several micrometres in length (Klemm et al. 2011, Lavoine et al. 2012, Abdul Khalil et al. 2014). They also have a very high surface area, in the range 170-246 m²g⁻¹, (as measured from a nanocellulose and polypyrrole aerogel composite (Carlsson et al. 2012)).

Nanocelluloses can be produced from cellulose pulp using pure mechanical or combined chemical or enzymatic and mechanical treatments. The chemical and enzymatic pretreatments reduce the energy needed for individualization of the nanofibrils. These treatments typically reduce the hydrogen bonds and/or add a repulsive charge, or else reduce the DP or the amorphous part between the individual nanofibrils (Lavoine et al. 2012). One of the most widely used chemical pretreatment is TEMPO (2,2,6,6 tetramethyl-1-piperidinyloxy)-mediated oxidation,
which selectively converts the C6 primary hydroxyl groups of the cellulose to carboxylate groups via aldehyde groups under alkaline aqueous conditions using catalytic amounts of TEMPO (Saito & Isogai 2005, Isogai et al. 2011, Lavoine et al. 2012). As a result, the cellulose fibre structure can easily be disintegrated to individual nanofibrils due to repulsive forces among the ionized carboxylates (Lavoine et al. 2012).

Another potential chemical oxidation pretreatment reaction for the production of nanocelluloses is periodate oxidation. In this reaction the C2 and C3 bonds of cellulose are selectively cleaved, yielding 2,3-dialdehyde cellulose, which can be further derivatized with functional groups such as carboxylic acids (Kim & Kuga 2001; Liimatainen et al. 2012b), sulphonic groups (Rajalaxmi et al. 2010, Liimatainen et al. 2012a, Liimatainen et al. 2013b) or imines (Sirviö et al. 2011a).

Only a few previous studies of the use of nanocelluloses as water chemicals exist and they mainly address adsorption applications. TEMPO-oxidized nanocelluloses have been used for the adsorption of various metals from aqueous solutions, most efficiently with lead, calcium and silver (Saito & Isogai 2005). Succinoyl anhydride-modified mercerized nanocellulose (Hokkanen et al. 2013) and amino-modified nanocelluloses (Hokkanen et al. 2014) showed high efficiency in the removal of metal ions, with good regeneration ability, while Kardam et al. (2014) achieved improved heavy metal adsorption capacity subjecting rice straw cellulosics to acid hydrolysis, which produced rod-like cellulose nanocrystals. Yu et al. (2013) used carboxylated cellulose nanocrystals for the adsorption of heavy metals with good results, as adsorption was fast, with high capacity, and the adsorbent was easy to regenerate. In flocculation applications, TEMPO-oxidized nanocelluloses with CPAM were used to flocculate kaolin clay suspensions, whereupon relative turbidity decreased greatly and the resulting flocs were stronger than with CPAM alone (Jin et al. 2014).
1.4 Aims of the present work

The aim of this work was to address the feasibility and performance of functionalized nanocelluloses in wastewater treatment processes. The focus was on solids separation and metal adsorption in particular.

1) The first target was to investigate the flocculation performance of various anionic nanocelluloses in the coagulation-flocculation treatment of municipal wastewater and to examine the morphology and strength of the resulting flocs.

2) Secondly, the synthesis of cationic nanocellulose and its aggregation performance in a kaolin clay mineral solution was investigated.

3) Finally, the adsorption of Pb (II) from diluted aqueous solutions with synthetized anionic nanocelluloses was studied.
2 Materials and methods

2.1 Materials

Bleached birch (*Betula pendula*) chemical kraft wood pulp obtained in dry sheets was used as the cellulose raw material for synthesizing anionic and cationic nanocelluloses (ADACs, CDACs and DCCs) for use as flocculants after disintegration in deionized water. The polysaccharide content of the pulp was determined using high-performance anion exchange chromatography (HPAEC-PAD) (Zuluaga et al. 2009), the lignin content using the TAPPI-T 222 om-02 standard and the extractive content using the SCAN-CM 49:03 standard. The cellulose content of the pulp was 74.8% and the hemicellulose (xyan and glucomannan) content was 24.7%. The amount of lignin was 0.4% and that of acetone-soluble extractives 0.08%. The average (length-weighted) length and width of the pulp fibres, as determined with a Metso FiberLab image analyzer, were 0.90 mm and 19.0 μm, respectively. The fibre fines content, as given by a L&W STFI Fibermaster analyzer (Sweden), was 3.4%.

Wheat straw (*Triticum aestivum L.*) chemical nonwood pulp obtained in dry sheets was used for synthesizing anionic nanocelluloses (WADAC) for use as adsorbents after disintegration in deionized water. The pulp was fractionated into fines and fibre fractions using a pressure screen, and the fines fraction (39% w/w of the whole pulp) was fractionated further into two fractions according to density and size differences using a hydrocyclone. These two fractions, i.e. the hydrocyclone overflow (Fines 1) and underflow (Fines 2), were thickened by settling and used as raw materials for fabricating the nanocellulose. The silicate, hemicellulose and lignin contents of the pulp were determined using the ISO 1762, TAPPI -T- 212 and TAPPI-T- 222 standards, respectively. The physical parameters of the fine fractions were measured with a Metso FiberLab image analyzer (Finland). The chemical compositions and physical parameters of the wheat pulp fine fractions are shown in Table 1.

<table>
<thead>
<tr>
<th>Fines</th>
<th>Cellulose [%]</th>
<th>Hemicelluloses [%]</th>
<th>Silicates [%]</th>
<th>Lignin [%]</th>
<th>Length (l) [μm]</th>
<th>Width [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fines1</td>
<td>81</td>
<td>15</td>
<td>3</td>
<td>1</td>
<td>260</td>
<td>14.4</td>
</tr>
<tr>
<td>Fines2</td>
<td>70</td>
<td>14</td>
<td>9</td>
<td>7</td>
<td>260</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Table 1. Chemical compositions and physical parameters of the wheat pulp fine fractions.
All the chemicals used in the synthesis and characterization of the nanocellulose materials were p.a. grade and obtained from Sigma-Aldrich (Germany). They were used without any further purification. The chemicals used to prepare the buffers for charge density measurement by polyelectrolyte titration were 0.1/1 M NaOH and HCl (Merck, Germany), NaH₂PO₄ (Sigma-Aldrich, Germany), NaCl (Merck, Germany), CH₃COOH (Merck), NaCH₃COO (Oy FF Chemicals, Finland), NaH₂PO₄ (Fluka, Germany), NaHCO₃ (Merck, USA), Na₂CO₃ (J.T. Baker, USA) and NaNO₂ (Sigma-Aldrich, Germany), all p.a. grade and used as received. Deionized water was used throughout the work.

PIX-105 (ferric sulphate, Fe₂(SO₄)₃) and Fennopol K1369 (cationic polyacrylamide) were obtained from Kemira, Finland, and were used in the experiments as an inorganic coagulant agent and a reference flocculant. These chemicals are commonly used in coagulation-flocculation wastewater treatment plants. The municipal wastewater samples were obtained from a Finnish activated sludge plant (in Oulu) after the screen phase. The process scheme for the wastewater treatment plant is presented in Fig. 7 and the characteristics of the wastewater samples in Table 2.

Fig. 7. Process scheme for the Oulu wastewater treatment plant (Oulun vesi 2005, ©Oulun vesi 2015).
Table 2. Characteristics of the samples obtained from the municipal wastewater treatment plant.

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>TSSa [mg dm⁻³]</th>
<th>TSb [mg dm⁻³]</th>
<th>pH</th>
<th>Conductivity [µS cm⁻¹]</th>
<th>CODc [mg dm⁻³]</th>
<th>Turbidity [NTU]</th>
</tr>
</thead>
<tbody>
<tr>
<td>water I</td>
<td>368</td>
<td>865</td>
<td>6.97</td>
<td>810</td>
<td>435</td>
<td>158</td>
</tr>
<tr>
<td>water II</td>
<td>404</td>
<td>897</td>
<td>6.92</td>
<td>1600</td>
<td>727</td>
<td>156</td>
</tr>
<tr>
<td>water III</td>
<td>692</td>
<td>1134</td>
<td>7.29</td>
<td>909</td>
<td>749</td>
<td>156</td>
</tr>
<tr>
<td>water IV</td>
<td>649</td>
<td>1272</td>
<td>7.14</td>
<td>1070</td>
<td>879</td>
<td>215</td>
</tr>
<tr>
<td>water V</td>
<td>485</td>
<td>983</td>
<td>7.19</td>
<td>986</td>
<td>848</td>
<td>189</td>
</tr>
</tbody>
</table>

a) Total suspended solids (SFS-EN 872); b) Total solids (SFS 3008:1990); c) Chemical oxygen demand (ISO 15705:2002)

Kaolin clay was supplied as a dry powder (J.M. Huber, Finland), from which a water slurry (pH 7.2) with a solids content of 40% was prepared with deionized water for the flocculation experiments. The particle size of the kaolin was 1.4 µm, as obtained from a Sedigraph (D₅₀ value), and its surface area was 12 m²g⁻¹, as measured by the Brunauer-Emmet-Teller (BET) method. The zeta potential and electrophoretic mobility of the kaolin as measured in this suspension with a Coulter Delsa 440 Electrophoretic Light Scatter Analyzer (USA) were -29.0 mV and -2.2 µms⁻¹/Vcm⁻¹, respectively.

2.2 Fabrication of the functionalized nanocelluloses

To fabricate the functionalized nanocelluloses, the cellulose raw material was first chemically pretreated (except WADAC, which was first disintegrated to a nano-scale) and then mechanically disintegrated to a nano-scale using high-pressure homogenization. The celluloses were functionalized using two-step reaction paths based on regioselective oxidation. In the first reaction step, the vicinal hydroxyl groups at positions 2 and 3 in the cellulose were oxidized to aldehyde groups with sodium metaperiodate to produce dialdehyde cellulose (DAC) (Fig. 8). The aldehyde content of the DAC was then determined using an oxime reaction according to a previously reported procedure (Sirviö et al. 2011b) (Table 3). The second reaction steps and liberation of the nanocelluloses from the pretreated celluloses are described below.
2.2.1 Synthesis of the anionic dicarboxyl acid nanocellulose (DCC) flocculant

Anionic dicarboxyl acid cellulose (DCC) derivatives with variable charge densities (DCC I-V) were synthesized from DAC using chlorite oxidation, as described elsewhere (Liimatainen et al. 2012b) (Fig. 9). Conductometric titration was used to analyse the number of anionic groups in the cellulose, using a previously described procedure (Katz et al. 1984, Rattaz et al. 2011).

The periodate and chlorite-oxidized celluloses were suspended in deionized water at a consistency of 0.5%, and the pH of the suspensions was adjusted to approximately 7.5 using dilute NaOH. The suspended celluloses were converted to nanofibrils using a two-chamber high-pressure homogenizer (Invensys APV-2000, Denmark) of a pressure of 250–950 bar. The suspensions were passed through the homogenizer one (DCC V), three (DCC II-IV), or four times (DCC I) until clear, gel-like samples were obtained.

2.2.2 Synthesis of the anionic sulphonated nanocellulose (ADAC) flocculant

Anionic sulphonated cellulose (ADAC) derivatives, with variable charge densities (ADAC I-IV) were synthetized from the DAC using a sulphonation reaction with
sodium metabisulphite (Fig. 10). The treated cellulosics were then suspended in deionized water at a consistency of 0.5% and converted to nanofibrils, as described above in synthesis of DCCs. ADAC I-III were fed through a homogenizer 5 times and ADAC IV 3 times until clear, gel-like samples were obtained. Details of the reaction conditions are presented in Liimatainen et al. (2013b). The numbers of anionic groups were analysed as described for the synthesis of DCCs.

Fig. 10. Periodate oxidation of cellulose followed by the bisulphite sulphonation reaction.

2.2.3 Production of anionic sulphonated nanocellulose (WADAC) adsorbents from wheat fines

To produce sulphonated wheat fines nanocelluloses (WADACs), functionalization was conducted after the disintegration of the wheat fines (Fines 1 and 2) to a nanoscale. The fines fractions were first suspended in deionized water with a consistency of 0.5% and then converted to nanofibrils (NFC 1 and 2) using a two-chamber high-pressure homogenizer (Invensys APV-2000, Denmark) with a pressure of 400–900 bar. Periodate oxidation followed immediately by sodium metabisulphite sulphonation was used to sulphonate the nanofibrils (WADAC 1 and 2). The suspensions were centrifuged after 72 hours of the sulphonation reaction, which was conducted at room temperature in an aqueous solution, and were washed until the conductivity of the suspensions was < 20 µScm⁻¹. The anionic charge density of the samples was analysed as described above.

2.2.4 Synthesis of the cationic quaternized (CDAC) nanocellulose flocculant

The cationic quaternized (CDAC) cellulosics with variable charge densities were synthetized from DAC materials using Girard’s reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT) at pH 4.5 for 72 h at 20 °C (Fig. 11). The
suspensions were passed through a homogenizer (Invensys APV-2000, Denmark) at 400-680 bar 3 times until clear nanocellulose gels were obtained. Details of the reaction conditions are presented in Paper III.

The amount of cationic groups was calculated from the nitrogen content of the products, as determined with a Thermo Scientific FLASH 2000 Series CHNS/O Analyzer (USA).

The reaction conditions used in cellulose functionalization, numbers of passes through homogenizer during nanofibrillation and the charge densities of the synthetized nanocelluloses are summarized in Table 3.
Table 3. Periodate oxidation parameters and aldehyde content after the first step in the reaction, the reaction time of the second step, number of passes through the homogenizer and amounts of anionic/cationic groups produced.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time of first step [min]</th>
<th>Reaction temperature [°C]</th>
<th>Aldehyde content [mmol g(^{-1})]</th>
<th>Reaction time of second step [h]</th>
<th>Passes through homogenizer</th>
<th>Anionic/cationic(^b) groups [mmol g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCC I</td>
<td>15</td>
<td>55</td>
<td>0.36</td>
<td>48</td>
<td>4</td>
<td>0.38a</td>
</tr>
<tr>
<td>DCC II</td>
<td>30</td>
<td>55</td>
<td>0.61</td>
<td>48</td>
<td>3</td>
<td>0.69a</td>
</tr>
<tr>
<td>DCC III</td>
<td>60</td>
<td>55</td>
<td>0.95</td>
<td>48</td>
<td>3</td>
<td>0.75a</td>
</tr>
<tr>
<td>DCC IV</td>
<td>120</td>
<td>55</td>
<td>1.31</td>
<td>48</td>
<td>3</td>
<td>1.20a</td>
</tr>
<tr>
<td>DCC V</td>
<td>180</td>
<td>55</td>
<td>1.68</td>
<td>48</td>
<td>1</td>
<td>1.75a</td>
</tr>
<tr>
<td>ADAC I</td>
<td>60</td>
<td>55</td>
<td>0.95</td>
<td>48</td>
<td>3</td>
<td>0.20a</td>
</tr>
<tr>
<td>ADAC II</td>
<td>60</td>
<td>55</td>
<td>0.95</td>
<td>72</td>
<td>5</td>
<td>0.36a</td>
</tr>
<tr>
<td>ADAC III</td>
<td>120</td>
<td>55</td>
<td>1.31</td>
<td>72</td>
<td>5</td>
<td>0.51a</td>
</tr>
<tr>
<td>ADAC IV</td>
<td>120</td>
<td>55</td>
<td>1.31</td>
<td>72</td>
<td>3</td>
<td>0.51a</td>
</tr>
<tr>
<td>WADAC I</td>
<td>180</td>
<td>55</td>
<td>na</td>
<td>72</td>
<td>8</td>
<td>0.41a</td>
</tr>
<tr>
<td>WADAC II</td>
<td>180</td>
<td>55</td>
<td>na</td>
<td>72</td>
<td>8</td>
<td>0.45a</td>
</tr>
<tr>
<td>CDAC I</td>
<td>180</td>
<td>55</td>
<td>1.68</td>
<td>72</td>
<td>3</td>
<td>1.10a</td>
</tr>
<tr>
<td>CDAC II</td>
<td>180</td>
<td>55</td>
<td>2.20</td>
<td>72</td>
<td>3</td>
<td>1.27a</td>
</tr>
<tr>
<td>CDAC III</td>
<td>180</td>
<td>75</td>
<td>2.84</td>
<td>72</td>
<td>3</td>
<td>1.53a</td>
</tr>
<tr>
<td>CDAC IV</td>
<td>180</td>
<td>75 + LiCl</td>
<td>3.83</td>
<td>72</td>
<td>3</td>
<td>2.25a</td>
</tr>
</tbody>
</table>

\(a\) Anionic charge density analysed by conductometric titration (Katz et al. 1984, Rattaz et al. 2011).

\(b\) Cationic charge determined by elemental analysis.
2.3 Characterization of the resulting nanocelluloses

2.3.1 Size distribution

Chromatographic washing was used to divide the particles in the nanocellulose samples into four size categories. The principle and theory of tube flow fractionation is presented in more detail in Laitinen (2011). The samples were washed in a long plastic tube (diameter 4 mm) with 1000 ml of deionized water for 108 s at a flow rate of 7.5 ml/s. Since the particles flow at different average velocities in this tube according to their size, so that the largest ones tend to stay in the middle of the tube longer given a faster flow, it is these particles that emerge first at the end of the long tube (Laitinen 2011) (Fig. 12). In this case, therefore, a 5 ml sample at a consistency of 0.1% was injected into the tube at a constant water flow, and four size categories were obtained by taking samples after 60, 77, 86 and 95 s (Fig. 12). The largest particles in the washed particle-water suspension were visualized with a charge-coupled camera (CCD) (resolution 1.6 µm) in a small cuvette, and the amount of material in the different categories was measured by filtration on a membrane (retention 0.2 µm) followed by weighing. Fractions were also collected for further analysis by field emission scanning electron microscopy (FESEM).

Fig. 12. Principle of the chromatographic washer.
2.3.2 Charge density (CD) of the nanocelluloses measured by polyelectrolyte titration

The polyelectrolyte titrations were performed at a solids content of 0.1% using a Mütek PCD 03 particle charge detector (USA). The samples were subjected to sonication for 60 min, filtered through a 1 µm membrane and mixed with the appropriate buffer. The anionic samples were titrated with cationic poly DADMAC (Poly(dimethyl diallylammonium)chloride) (1 mequiv. dm\(^{-3}\)) and the cationic samples by adding aqueous PES-Na (sodium polyethenesulphonate) (1 mequiv. dm\(^{-3}\)) while monitoring the sign of the sample charge.

2.3.3 Morphology of the nanocelluloses

A FESEM Zeiss Ultra Plus (Germany) electron microscope was used to study the morphology and size of the chromatographically washed nanofibrils in various fractions. As a pretreatment, the samples were filtered to a polycarbonate membrane with 0.2 µm pores followed by rapid freezing with liquid nitrogen and freeze-drying in a vacuum overnight. The dried samples were sputter-coated with platinum. A voltage of 10 kV and a working distance of 5 mm were used when taking the samples.

2.4 Coagulation-flocculation experiments

The flocculation performance of the anionic nanocelluloses was evaluated by measuring the residual turbidity and COD of the settled wastewater after the coagulation-flocculation treatment using a procedure similar to standard jar testing. The wastewater (100 ml) was treated using a ferric coagulant or ferric coagulant and anionic nanofibrils. The experiments were conducted by adding a constant dose of ferric coagulant (25 mg dm\(^{-3}\) after the dosage had been optimized) to a beaker containing the wastewater and stirring the suspension with a magnetic stirring bar at 200 rpm for 3 min at room temperature. After the coagulation treatment, the nanocellulose solution (2.5–50 mg dm\(^{-3}\)) was added to the wastewater, and the suspension was stirred at 40 rpm for 15 min. Finally, the suspension was allowed to settle for 30 min at room temperature. The turbidity of the supernatant was measured with a Hach Ratio XR turbidimeter (model 43900) (USA) and its COD from standardized test tubes (Hach) with a Hach Lange DR 2800 spectrophotometer (USA).
2.4.1 Morphology and strength of the flocs

A constant dose of ferric coagulant (25 mg dm\(^{-3}\)) was added to a beaker containing 1000 ml wastewater and the suspension was stirred with a magnetic stirring bar at 200 rpm for 3 min at room temperature. After the coagulation treatment, the nanocellulose (ADAC or DCC) solution (5 or 10 mg dm\(^{-3}\)) was added to the wastewater and the suspension was stirred at 40 rpm for 15 min.

The morphology and strength of the flocs were determined with a custom-built MOFI (floc measurement environment) analyzer that includes imaging of the sample in a cuvette with a CCD camera (Fig. 13). Two hundred millilitres of flocculated wastewater were diluted to 1800 ml with deionized water in the mixing unit (Fig. 13). After dilution, the sample was pumped through a 5 mm cuvette, where the flocs were visualized with a CCD camera (resolution 3.6 \(\mu\)m). The sample was recirculated to the mixing unit using a centrifugal pump with a rotational speed of 1400 rpm during the experiments, and the experiments were continued for 90 s. In this method, the flocs break due to the pumping and the hydrodynamic forces of recirculation. Approximately 800–1000 images were taken of every sample, each image containing approximately 80 flocs. Thus, on average, more than 72,000 individual flocs were analyzed in every sample.

![Fig. 13. Schematic illustration of the floc measurement environment (MOFI) (Paper II, ©Elsevier 2015).](image)

The morphology of the flocs was analyzed from the CCD images with the automated image analysis program presented by Koivuranta et al. (2013). This
image analysis program calculates specific particle features for each image, e.g. the total particle area, number of particles and various shape factors such as the form factor and roundness. Shape factors are calculated only for particles of more than 100 µm² in size, because the boundaries of small particles are usually difficult to define at the given limits of resolution. The form factor (FF) is affected by the irregularity or roughness of the object’s boundary, being 1.0 for a perfect circle and below 1.0 for any other shape. Objects with irregular boundaries have a longer perimeter per unit of surface area and therefore have lower form factors. The form factor is calculated from Eq. (2) (Russ 1990, Costa et al. 2013, Koivuranta et al. 2013):

\[ FF = \frac{4\pi \times \text{area}}{\text{perimeter}^2}. \] (2)

Roundness (RO) (Eq. 3) is defined as the ratio between the area of an object and the area of a circle with a diameter equal to the object’s length (Russ 1990, Costa et al. 2013, Koivuranta et al. 2013):

\[ RO = \frac{4\pi \times \text{area}}{\pi \times \text{length}^2}. \] (3)

Roundness (RO) is 1.0 for a perfect circle.

2.5 Flocculation of the kaolin clay suspension with cationized nanocelluloses

The flocculation performance of the cationized nanocelluloses (CDACs) was evaluated by flocculating suspensions of a model kaolin filler and determining its residual transmission after centrifugation at 400 rpm for 300s at 20°C with an analytical centrifuge (LUMIfuge, L.U.M. GmbH, Germany) consisting of a light source, a rotor above which the sample cells containing the suspension were horizontally positioned and a CCD line sensor below the rotor. This centrifuge simultaneously measures light transmission at 800 nm over the plastic sample cells as a function of time and position, so that local alterations in particle concentration and the position of the solid-liquid interface during separation can be detected by changes in light transmission (von Homeyer et al. 1999). Aggregation in the suspensions is indicated by increases in the sedimentation rate and residual transmission.
2.6 Adsorption experiments

The adsorption experiments were performed in batch mode with a model sample of water containing lead. In each experiment a 25 g batch of lead(II)nitrate (Pb(NO₃)₂) (containing 0.24 - 6.38 mmol/l of lead) and 50 mg of WADAC nanocellulose were mixed. The pH of the suspensions was adjusted using HCl or NaOH, while 5 ml of a 0.1 M acetate buffer was added to keep the pH constant value at 5. The suspensions were agitated for 20 hours at room temperature, after which they were centrifuged for 20 minutes at 15 000 xg and a temperature of 4°C. The lead concentrations of the solutions were analyzed using a atom absorption spectrometer (AAS, Perkin Elmer 4100, USA).

The amount of lead adsorbed per unit mass of nanocellulose adsorbent \( q_e \) (mmol/g) was calculated as follows:

\[
q_e = \frac{C_i - C_e}{m} V
\]  

where \( C_i \) and \( C_e \) are the initial and equilibrium lead concentrations (mmol/L) and \( m \) and \( V \) are the weight of the absorbent (g) and the volume of the solution (L).

2.6.1 Adsorption isotherm models

Langmuir and Freundlich isotherms were used to model the adsorption behaviour of the sulphonated nanocelluloses. The Langmuir model is as follows (Langmuir 1918):

\[
q_e = \frac{Q_0bC_e}{1+bC_e}
\]

where \( q_e \) (mmol/g) and \( C_e \) (mmol/L) are the adsorbed metal ions on the adsorbent and the metal ion concentration in the solution at equilibrium, respectively. \( b \) (L/mmol) is a constant that is related to the affinity of the binding sites. \( Q_0 \) (mmol/g) is known as the Langmuir constant, which represents the monolayer sorption capacity, i.e. the maximum amount of metal ions per unit weight of adsorbent that is needed to form complete monolayer coverage (Gadd 2009, Gupta & Babu 2009, Hubbe et al. 2011).

The Freundlich model may be expressed as follows (Gupta & Babu 2009, Hubbe et al. 2011):

\[
q_e = K_F C_e^n
\]
where $K_F$ (mg$^{1-n}$/g L$^n$) and n (dimensionless) represent the Freundlich constants. $K_F$ is indicative of the relative adsorption capacity, whereas $n$ is a measure of the nature and strength of the adsorption process and the distribution of active sites (Gadd 2009, Hubbe et al. 2011). The smaller the value of $n$, the greater the heterogeneity. If $n = 1$, all the surface sites are equivalent, if $n < 1$, the bond energies increase with increasing surface density, and if $n > 1$, the bond energies decrease with increasing surface density (Nameni et al. 2008, Gadd 2009, Hubbe et al. 2011).
3 Results and discussion

3.1 Characteristics of nanocelluloses

3.1.1 Size and morphology of the nanocelluloses

ADAC and DCC

The mass proportions of size fractions obtained from the chromatographic washer for the anionized nanocelluloses (DCC and ADAC) are shown in Fig. 14 and typical particles present in the various fractions in Fig. 15. Fraction 1 (FR 1) contained the largest particles, and thus mainly non-fibrillated material and flocs particles. The second fraction (FR 2) contained fibrillated material, but still mainly bunches of fibrils. The measured widths of the particles in FR 2 as detected in the FESEM images ranged from approximately 20 nm to approximately 60 nm while the lengths were assumed to be some tens of micrometres. FR 3 contained highly fibrillated particles that were approximately 4 to 10 nm wide and several micrometres long. FR 4 contained the finest material and had rounder particles with a lower aspect ratio than FR 2 or FR 3. The ADACs contained more fibrillated material (FR2 and FR3) and less large particles (FR1) than the DCCs (except for ADAC I), due to the higher number of passes through the homogenizer. A higher charge also induces degradation in the homogenizer, as seen in the higher fibril content of the more oxidized samples (Fig. 14).

Fig. 14. Mass proportions of the size fractions in the DCC (a) and ADAC (b) nanocelluloses obtained from the chromatographic washer (Paper I, ©Elsevier 2015).
The mass proportions of the size fractions of the unmodified nanocelluloses (NFC 1 and 2), sulphonated nanocelluloses (WADAC 1 and 2) and fines fractions (Fines 1 and 2) of wheat pulp are shown in Fig. 16. Fraction 1 (FR 1) mainly contained non-fibrillated material, and therefore the largest particles, as seen in the non-fibrillated fines samples (Fines 1 and 2). Moreover, FR 1 also included flocs formed of individual micro- and nanofibrils. The fibrillated samples NFC 1 and 2 had a similar fractional composition to that of the non-fibrillated samples after 8 passes through the homogenizer, but closer examination by FESEM imaging (Fig. 17) revealed that the micro- and nanofibrils formed larger flocs, and consequently they appeared in FR 1. Nanofibril flocculation decreased after sulphonation treatment due to the increased charge density of the cellulose, which increased the repulsion between the particles and reduced the amount of FR 1.
CDAC

FESEM analysis confirmed that the cationic celluloses had efficiently disintegrated to nanofibrils (CDAC) (Fig.18) of an estimated width ranging from 10 to 50 nm and several micrometres in length. The CDACs also possessed very high transmittance values at a consistency of 0.1%, in the range 400-800 nm, which indicates that these compounds were highly transparent. These findings also supported the FESEM results, which indicated that the CDAC samples were highly fibrillated and the number of larger bundles of fibrils was low.

3.1.2 Charge density of the nanocelluloses

The apparent CDs of the DCC I-V and CDAC I-IV nanocelluloses in the pH range 3-10, as determined by polyelectrolyte titration, are shown in Fig. 19. The apparent anionic charge density of the DCCs increased towards neutral conditions and remained quite constant after a pH of about 7. These DCC curves are well
compatible with the dissociation constant expected for uronic acids (pK = 3.5-4) (Kohn 1973, Kohn & Kovac 1978, Laine et al. 1994). DCCs IV and V, with higher numbers of carboxyl groups, showed greater charge density changes from acidic to neutral conditions than did the other DCCs, but all the DCC flocculants showed constant CDs below pH 6-8, i.e. in the range that normally prevails in activated sludge wastewater treatment. The charge densities of the quaternized cationic nanocelluloses were stable in the pH range studied here, so that only a decrease in CD of approximately 0.1 mequiv.g⁻¹ was observed. The CDs obtained by polyelectrolyte titration under neutral conditions were substantially lower than the carboxyl group content values obtained by conductometric titration (Table 3) or corresponding values obtained from elemental analysis (Table 3). This may be due to the high MW of the titrant polymer, which sterically restricted the availability of carboxyl or quaternary ammonium groups in the cellulose. The titrant-cationic cellulose complexes formed in the CDAC may also appear in ratios other than the stoichiometric charge ratios.

**Fig. 19.** Apparent CDs of the DCCs (a) and CDACs (b) as a function of pH (Paper I and III, ©Elsevier 2015).

### 3.2 Solids removal

Solids removal with anionic nanocelluloses (DCCs and ADACs) was tested by means of combined coagulation-flocculation treatments in which a cationic ferric coagulant was added to municipal wastewater samples before the addition of an anionic flocculant. The cationic nanocellulose CDAC was used as a flocculant without any coagulation aid to flocculate kaolin suspensions.
3.2.1 Coagulation-flocculation of municipal wastewater with anionic nanocelluloses (Papers I-II)

Performance of pure coagulant

The optimization of the coagulant (ferric sulphate) dosage in the coagulation-flocculation experiments is shown in Fig. 20. The reduction in turbidity started after the addition of about 50 mg dm\(^{-3}\) of ferric sulphate and increased up to a dose of 250 mg dm\(^{-3}\) (given a final turbidity removal of approximately 83%). The same trend was seen in COD reduction, although the process was not as efficient as in the case of turbidity (final COD reduction of 50-55%). The dose of coagulant chosen for the coagulation-flocculation experiments was 25 mg dm\(^{-3}\).

![Fig. 20. Reductions in turbidity (a) and COD (b) achieved in wastewater samples I-III after coagulation treatment as a function of the dose of coagulant (ferric sulphate). The settling time was 30 min.](image)

Performance of DCCs

The flocculation performance of the DCCs in combined coagulation-flocculation treatment (ferric sulphate and DCC) is shown in terms of turbidity and COD reduction as a function of DCC dosage in Fig. 21. The results indicate that all the DCCs were able to flocculate wastewater efficiently (turbidity reduction of 40-80% and COD reduction of 40-60%). The effective doses of the DCCs were similar to those of the commercial cationic polymer (CPAM) used as a reference flocculant. The reference polymer showed 14-40% higher turbidity reduction efficiency than the DCCs (Fig. 21a), but the DCC flocculants showed a similar level of...
performance in COD reduction (Fig. 21b). The optimum improvements were achieved with moderately low doses of DCC flocculants (2.5-5 mg dm⁻³).

![Fig. 21. Reductions in turbidity (a) and COD (b) in water sample I after coagulation-flocculation treatment as a function of the dose of DCC flocculant and the reference polymer Fennopol K1369. The dose of coagulant (ferric sulphate) was 25 mg dm⁻³ (Paper I, ©Elsevier 2015).]

**Performance of ADACs**

The flocculation performance of the ADAC nanocellulose flocculants in the combined coagulation-flocculation treatment (ferric sulphate and ADAC) of municipal wastewater (Water III) is shown in terms of turbidity and COD reduction as a function of the flocculant dose in Fig. 22. The performance of the ADACs was even better in turbidity removal at small doses (2.5 mg dm⁻³) than was that achieved with the DCCs in relation to the performance of the reference flocculant. The performance was similar to or better than that of the commercial reference polymer. The reason behind the more efficient performance of the ADACs may be that the sulphonate groups attached themselves more efficiently to the cationic patches of the iron coagulant than did the carboxyl acid groups of the DCCs. The flocculation results show that the higher anionic charge of the ADACs provided a better result in terms of turbidity reduction (Table 3), while the effect of the size of the flocculent was not as clear.
Fig. 22. Reductions in turbidity (a) and COD (b) in water II after coagulation-flocculation treatment as a function of the dose of ADAC flocculent and reference polymer Fennopol K1369. The dose of coagulant (ferric sulphate) was 25 mg dm⁻³ (Paper II, ©Elsevier 2015).

The flocculation results for the DCCs and ADACs also showed that the same decrease in turbidity and COD was achieved in combined coagulation-flocculation treatment with a nanocellulose dose of 25 mg dm⁻³, while a dose from 200 to 250 mg dm⁻³ was needed with coagulant alone. Thus a considerable decrease in the total chemical load was achieved.

The flocculation performance of the combinations of coagulant and nanocelluloses (ADACs and DCCs) was investigated in the pH range 6-8 (Paper I). These results taken together with the charge density results (Fig. 19) indicated that the anionic nanocellulose flocculants (ADACs and DCC) were effective throughout this pH range and no inactivation occurred.

3.2.2 Flocculation mechanism of the anionic nanocelluloses

While the soluble reference polymer yielded large floats of airy flocs which were drifting in the water, the DCCs and ADACs formed small, tight flocs which slowly settled on the bottom of the container.

The anionic nanofibrils were unable to flocculate anionic dirt material from the municipal wastewater without assistance from a cationic coagulant, due to charge repulsion, so that it was important to ascertain the right coagulant dose for charge neutralization. It is likely that the positively charged ferric species provided cationic patches on the surface of the dirt particles (Tripathy & De 2006, Bolto &
and that the elongated anionic nanofibrils connected with coagulated aggregates via these cationic patches (Fig. 23). Jin et al. (2014), who flocculated kaolin clay with CPAM and TEMPO-oxidized nanocelluloses, similarly found that CPAM resulted in large, loose, easily breaking flocs whereas the CPAM-TEMPO-nanocellulose combination resulted in smaller, denser and stronger flocs (Jin et al. 2014).

**Fig. 23. Proposed flocculation mechanism for anionic nanocelluloses.**

It is generally known that the most effective soluble polymers for bridging are those possessing a high molecular weight (Ghimici & Nichifor 2012), but the charge density can also have a considerable influence on bridging performance (Singh et al. 2000, Bolto & Gregory 2007, Ghimici & Nichifor 2010). In the case of the anionic nanofibrils, the influence of the CD was not so obvious. Presence of multivalent metal ions such as Fe$^{3+}$ may promote complexation of the metal with carboxylate groups on the polymer chain and cause an effective reduction in CD (Bolto & Gregory 2007), which can in turn reduce the efficacy of the flocculant. The sulphonic groups in ADAC probably have a higher affinity for the iron patches in the coagulant than do the carboxyl acid groups, which may explain the better flocculation performance of the ADACs as compared with the DCCs. Moreover, sulphonic group is likely to have a greater degree of ionization than the other functional groups in cellulose (e.g. hydroxyl or carboxyl groups), so that the electrostatic affinity of sulphonic groups for metals may be stronger (Krishnan & Anirudhan 2002, Dong et al. 2013).

### 3.2.3 Morphology and strength of the resulting flocs

The morphology and strength of the flocs in combined coagulation-flocculation treatment with ferric sulphate and anionic nanocelluloses were followed by means of a MOFI analyzer based on image analysis (Fig. 25). The particle size distribution
of the flocculated wastewater (Fig. 25a) showed that all the flocculants contained the same amount of the smallest flocs (< 25 µm), which is the size of those particles that do not settle easily. The largest flocs were clearly formed by the reference polymer, but they were not as round in shape as with the nanocellulose flocculants (Fig. 25b). Figure 25c shows the equivalent diameter for wastewater particles that had an area of over 100 µm², while in Fig. 25d all the particles were included in calculation of the mean area. Thus the mean area results may be said to be dominated by the effect of a few really large flocs of the reference polymer. The roundness and density of the flocs are the factors that have been observed previously to promote the efficiency of water treatment (Young & Edwards 2003, Schuler & Jang 2007). Of the nanocellulose flocculants, the ADACs formed the roundest flocs while the reference polymer had the most irregular ones, which easily broke up to form smaller round flocs (Fig. 24 and 25b–d), after which the reference polymer flocs were of a similar size to the nanocellulose flocs (Fig. 25c). Li et al. (2006) showed that floc rupture is caused by their surface erosion and large-scale fragmentation. The reference sample showed the largest differences in roundness, equivalent diameter and surface area values during breaking, which suggested that surface erosion and fragmentation affected floc breakage, whereas only minor changes in floc morphology were observed with the nanocellulose flocculants, indicating that more surface erosion existed than fragmentation. Natural polymers have previously been found to be shear-stable (Singh et al. 2000, Ghimici & Nichifor 2010), as was also seen with the nanocellulose flocculants during pumping (Fig. 25). Floc breakage depends on the strength of the floc when subjected to the tension, compression and shear forces that are present in turbulent flows and pumping situations in wastewater treatment plants (Yuan & Farnood 2010). In the MOFI analyzer the flocculated wastewater was centrifugally pumped through the imaging unit and circulated back into the mixing unit, thus constituting a floc measurement environment that gave a realistic view of floc breakage.

In addition, a higher dosage of the reference polymer produced larger and weaker flocs, whereas higher doses of DCCs produced even smaller flocs and higher doses of ADACs seemed to have no effect, so that the roundness (Fig. 25b) was slightly lower.
Fig. 24. Images obtained from the MOFI analyser. Flocs formed with the reference polymer and with the ADAC nanocellulose.

Fig. 25. Size distribution of the flocs formed with anionic nanocelluloses and the reference polymer in wastewaters IV and V (a), roundness of the flocs (b), their equivalent diameter (flocs over 100 µm²) (c), and the mean area of all particles (d) before and after floc breakage (dose of flocculants 5 or 10 mg dm⁻³) (Paper II, ©Elsevier 2015).
3.2.4 Flocculation of kaolin clay with cationic nanocelluloses (Paper III)

The flocculation performance of cationized nanofibrils (CDACs) was evaluated by flocculating kaolin clay model suspensions and determining their residual transmission after centrifugation. The flocculation performance of CDACs in terms of the residual transmission of the kaolin suspensions as a function of CDAC dosage is shown in Fig. 26. All the CDAC samples yielded flocculated kaolin suspensions at low dosages, as indicated by the increased transmissions of the suspensions. The lowest optimum dosage among the CDACs was achieved with CDAC IV, indicating that increased charge density promoted the flocculation of kaolin colloids.

![Fig. 26. Residual transmission of the kaolin clay suspensions after flocculation with cationic nanocellulose fibrils and analytical centrifugation (400 rpm for 300 s at 20°C and pH of 7.2) (Paper III, ©Elsevier 2015).](image)

The flocculation performance of the CDACs, evaluated over a pH range of 3-11 and a temperature range of 35-60°C (Paper III), maintained a constant high level from pH 3 to 9 for all the samples, supporting the charge density results (Fig. 19), but a slight decrease in flocculation was noted at pH 10.5 in the CDAC II and IV samples. This was probably due to the alkaline-induced degradation of the β-alkoxy fragmentation of the DAC backbone, as described earlier (Calvini et al. 2004).
3.2.5 Flocculation mechanism of cationic nanocelluloses

Cationic soluble flocculant polymers and inorganic coagulants are able to adsorb to oppositely charged particle surfaces and to neutralize charged surface groups, leading to particle aggregation (Das et al. 2013). It is likely that cationic nanofibrils are able to neutralize the anionic surfaces of kaolin clay, causing flocculation of the kaolin particles. The enhancement of flocculation as a function of the charge density of CDAC also indicates that charge neutralization was promoted as the amount of cationic charges increased (Fig. 26). Overdosing of cationic nanocelluloses, however, resulted in rapid charge reversal and restabilization of the kaolin particles (Fig. 26), which further supports the claims regarding charge neutralization mechanisms. No rapid restabilization that might refer to a bridging mechanism was observed with CDAC IV, so that it is possible that long fibrils may also adsorb to more than one particle, linking them together, in addition to achieving charge neutralization.

3.3 Metal adsorption

3.3.1 Adsorption of Pb(II) with WADACs (Paper IV)

A model aqueous suspension containing Pb (II) was used to investigate the adsorption performance of chemically modified (sulphonated, WADAC) and unmodified (NFC) nanocelluloses. The adsorption efficiency of these cellulosics was found to be poor below pH 4, indicating that the anionic binding sites of the adsorbents were protonated. An increase in pH increased the adsorption efficiency, although to avoid the precipitation of Pb, the pH of the solution was raised only to a maximum value of 5 in this study. Sulphonated nanocelluloses possess a large number of binding sites, due to the high surface area of the nanofibrils, and sulphonation further increases the number of binding sites and the accessibility of the nanofibrils, so that the diffusion of Pb(II) to active adsorption sites increases. The adsorption rate was extremely high at the beginning, indicating that Pb(II) was adsorbed by a readily available adsorption site (Dong et al. 2013, Hokkanen et al. 2014). It is likely that the degree of ionization of the sulphonic groups was higher than that of the others such as carboxyl or hydroxyl groups (Dong et al. 2013). Soft acid-like sulphur forms complexes with ligands having a covalent character rather than an ionic one (Gadd 2009), and at the beginning of Pb(II) adsorption to WADAC the ions are tied together with two ligands to form complexes. At low
concentrations all the Pb(II) ions present in the solution could interact with two binding sites, leading to a higher adsorption performance (Hokkanen et al. 2014). Another possible mechanism is ion exchange with an adjacent hydroxyl group, but as with many other bioadsorbent materials, there is also a possibility that both mechanisms may take part in adsorption, since there are several active groups present in the surface of the adsorbent (Gadd 2009, Hubbe et al. 2011).

The adsorption capacities of the nanofibrillated samples (NFC 1 and 2) and the nanofibrils after sulphonation (WADAC 1 and 2) are shown as a function of the equilibrium Pb(II) concentration of the solution in Fig. 27. It can be clearly seen that sulphonation significantly increased the affinity of Pb(II) for the nanocellulosics. In addition to the highest charge, the sulphonated nanofibrils also had the highest surface area, because the sulphonated groups reduced the aggregation of the nanoparticles (Figs. 16 and 17), which probably promoted adsorption. WADAC 2, which also had the highest charge density, had the best affinity for Pb(II) of all the samples.

![Fig. 27. Isotherms for the adsorption of Pb(II) to NFC and WADAC nanocellulosic adsorbents: a) the Langmuir model fitted to the data (dashed line) and b) the Freundlich model fitted to the data (dashed line) (Paper IV, ©Elsevier 2015).](image)

Langmuir and Freundlich isotherms were used to study the mechanism of Pb(II) adsorption in the samples, yielding the constants shown in Table 5. The regression coefficient indicates that the Langmuir isotherm model had a better fit than the Freundlich model, which in turn suggests that homogeneous monolayer adsorption takes place even when different adsorption sites are available on the surfaces of the sulphonated nanocellulosics. It is possible that Pb(II) ions may be bound with two
ligands to form large complexes, thus sterically hindering access to other binding sites.

The adsorption capacities, i.e. the values of $Q^0$ (Table 5), representing the maximum adsorption capacities of the sulphonated samples (0.9 mmol g$^{-1}$ for WADAC 1 and 1.2 mmol g$^{-1}$ for WADAC 2), were higher than those for many other adsorbents. The adsorption capacities of a Pb(II) ion with different lignocellulosic adsorbents and activated carbon have been reported to be below 0.5 mmol g$^{-1}$ (Hubbe et al. 2011), and higher capacities for Pb(II) adsorption have only been reported for certain specific aquatic plants (1.2 mmol g$^{-1}$), bacteria (2.7 mmol g$^{-1}$), algae (2.6 mmol g$^{-1}$) or fungi (1.3 mmol g$^{-1}$) (Hubbe et al. 2011). Chemical modifications such as mercerization and succinylation, 0.93-2.4 mmol g$^{-1}$ (Karnitz Jr et al. 2007, Gurgel et al. 2008, Gurgel & Gil 2009), phosphorylation, 0.55-3.08 mmol g$^{-1}$ (Klimmek et al. 2001, Vaughan et al. 2001) or sulphurization, 0.97 mmol g$^{-1}$ (Krishnan & Anirudhan 2002), have also been found to increase the adsorption capacities of lignocellulosic materials. The adsorption capacities obtained with sulphonated samples in this investigation are comparable to those reported for other chemically modified lignocellulose adsorbents.

Table 4. Isotherm constants and regression coefficients for Langmuir and Freundlich isotherms for the adsorption of Pb(II) to treated nanocellulose (NFC 1 and 2) and sulphonated nanocellulose (WADAC 1 and 2) adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q^0$ [mmol g$^{-1}$]</td>
<td>$R^2$</td>
</tr>
<tr>
<td>WADAC 1</td>
<td>0.9007</td>
<td>0.93</td>
</tr>
<tr>
<td>WADAC 2</td>
<td>1.2077</td>
<td>0.97</td>
</tr>
</tbody>
</table>

3.4 Feasibility of nanocelluloses as potential water chemicals

The key aspects for commercially viable nanocellulosic water chemicals are their performance and the costs of functionalization. Since this work showed functionalized cellulosics to achieve very good performance in solids removal and the adsorption of Pb (II), the main challenges are related to the economics of their production, and given that the cellulosic raw material doesn’t have to be pure cellulose pulp (wood or non-wood), the use of wastes or side-streams associated with different processes such as those used in pulp mills could be a viable option.
The first oxidation step in the production of functionalized celluloses was carried out here using periodate (IO₄⁻), which is expensive and harmful chemical, but it has also been shown that periodate can be regenerated efficiently with hypochlorite (Liimatainen et al. 2013a). Aqueous solutions obtained after 10 and 15 min of cellulose oxidation with periodate were regenerated with 100% conversion efficiency using 1.2–1.4 times the stoichiometric amount of hypochlorite. Moreover, the regenerated solutions possessed good oxidation performance, showing that periodate can be successfully regenerated using hypochlorite and supporting the assumption that it can be effectively recycled by this means when short oxidation times are used (Liimatainen et al. 2013a).

Of the functionalized nanocelluloses studied here, the sulphonated nanocelluloses showed especially good performance in the coagulation-flocculation treatment of municipal wastewater, as also in the adsorption experiments. Since sodium metabisulphite, which was used in the fabrication of these nanocelluloses, is a low-priced bulk chemical, these nanocellulosics are probably the most feasible options for further investigations.

Different production parameters that could be used in the fabrication of sulphonated nanocelluloses are presented in Table 5 and the calculated total costs of their production in Table 6. It has been assumed that the raw cellulose material comes from local sources (Table 6) and that low-cost side-streams are used. The yields of DAC after periodate oxidation and sulphonated cellulose after the metabisulphite reaction have both been estimated based on lab-scale experiments to be 90%. Over 98% of the periodate used is estimated to be recycled back to the process (Table 5), and also all of the washing water. A high excess of sodium metabisulphite was used in the lab-scale experiments, and 80-90% of the reagents ended up as waste (Table 5). Optimization of the sulphonation reaction would also reduce the amount of reagent required. Similarly, it was assumed here that half of the washing water used in the sulphonation reaction step could be recycled back into the process. Nanofibrillation of the cellulosics used for local wastewater treatment does not necessarily require high-capacity equipment. In fact, grinder-type equipment would probably be suitable for this purpose.
Table 5. Parameters of the production of sulphonated nanocellulose.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Yield [%]</th>
<th>Dry matter content [%]</th>
<th>Other</th>
<th>Washing step</th>
<th>Dry Content [%]</th>
<th>Water used [l/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periodate oxidation</td>
<td>90</td>
<td>1.0</td>
<td>Degree of periodate recycling &gt;98%</td>
<td>30</td>
<td>100 (recycled)</td>
<td></td>
</tr>
<tr>
<td>Sulphonation</td>
<td>90</td>
<td>1.0</td>
<td>80-90% of reagents end up as waste</td>
<td>20</td>
<td>100 (50% recycled)</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Costs of producing anionic nanocelluloses.

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost [k€/ton]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material (side-stream from a local pulp mill)</td>
<td>0.1</td>
</tr>
<tr>
<td>Process chemicals and their regeneration</td>
<td>0.8</td>
</tr>
<tr>
<td>Heat, electricity and water</td>
<td>0.4</td>
</tr>
<tr>
<td>Pre-treatments</td>
<td>0.2</td>
</tr>
<tr>
<td>Size reduction</td>
<td>0.2</td>
</tr>
<tr>
<td>Production costs</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Since the price of synthetic polymers such as PAM is approximately 1-4 k€/ton, the costs of producing sulphonated nanocelluloses from cellulosic side-streams of local sources (1.7 k€/ton) are reasonable and compatible with the prices of conventional flocculation chemicals. Even virgin cellulose pulp (0.5-0.7 k€/ton) could be a profitable option as a source of nanocellulosic water chemicals.
4 Conclusions

Functionalized nanocelluloses offer novel green alternatives for solids removal and heavy metal adsorption in water treatment processes. Nanocelluloses can be seen as promising candidates for replacing the current oil-derived synthetic water chemicals, and preliminary calculations of the costs of producing functionalized nanocelluloses indicate that these costs are reasonable and compatible with those of conventional flocculation chemicals.

Anionic nanocelluloses showed good performance in the treatment of municipal wastewater when combined with coagulation-flocculation treatment using a ferric coagulant. COD removal with dicarboxylic acid (DCC) and sulphonated (ADAC) nanocelluloses was similar to the performance of the commercial reference polymer at low dosages, and the performance of turbidity reduction with ADACs was also as good as with that achieved with the reference polymer, although the performance with DCCs was slightly inferior. The combined treatment nevertheless resulted in lower residual turbidity and COD in the settled suspension, with a highly reduced total chemical consumption with both anionic nanocelluloses relative to coagulation with ferric sulphite alone.

The wastewater flocs produced with the nanocellulose flocculants were smaller and rounder than those produced with the commercial reference polymer, but the flocs produced with anionic nanocelluloses were more stable under shear forces than those flocs produced with the reference polymer.

The cationic celluloses showed good flocculation performance with the model aqueous kaolin clay solutions. All of the CDACs resulted in pronounced aggregation of kaolin colloids and maintained effective flocculation performance over wide pH and temperature ranges.

In the case of adsorption, the sulphonation of nanofibrillated wheat straw pulp fines offered a potential route for obtaining a biosorbent for the recovery of metals from aqueous solutions. Pb(II) was efficiently adsorbed from a model solution by nanofibrillated and sulphonated fine cellulosics, while unmodified nanocelluloses exhibited poor adsorption capacities. The adsorption capacity of the former was 1.2 mmol/g at pH 5, which is comparable to the capacities of commercial adsorbents. The Langmuir isotherm model fitted the data better than did the Freundlich model for the adsorption of Pb(II) to treated wheat straw pulp fine adsorbents, which indicates that homogeneous monolayer adsorption takes place even when different adsorption sites are available on the surfaces of the sulphonated nanocelluloses.
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