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UNIVERSITY of OULU

FACULTY OF TECHNOLOGY

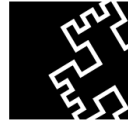
**THE FLOTATION RESPONSE OF QUARTZ USING  
AMINATED CELLULOSE NANOCRYSTALS AND  
COMMERCIAL COLLECTORS**

Saku Kimpimäki

ENVIRONMENTAL ENGINEERING

Bachelor's Thesis

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# TIIVISTELMÄ

## OPINNÄYTETYÖSTÄ Oulun yliopisto Teknillinen tiedekunta

Koulutusohjelma (kandidaatintyö, diplomityö) Ympäristötekniikan koulutusohjelma		Pääaineopinnojen ala (lisensiaatintyö)	
Tekijä Saku Kimpimäki		Työn ohjaaja yliopistolla Hartmann, R. M.Sc., Laitinen, O. Dr. (Tech.)	
Työn nimi Kvartsivaahdotus käyttämällä aminoitua kiteistä nanoselluloosaa ja kaupallisia kerääjiä			
Opintosuunta Kuitu- ja partikkelitekniikka	Työn laji Kandidaatintyö	Aika Helmikuu 2016	Sivumäärä 32 s.
Tiivistelmä <p>Selluloosa on yleisin luonnollinen polymeeri maapallolla, ja sillä on monia ominaisuuksia kuten, uusiutuvuus, biohajoavuus ja myrkyttömyys, joiden ansiosta eri mikro- ja nanoselluloosia pidetään potentiaalisina biopohjaisina kemikaaleina. Kiteiset nanoselluloosat (CNC:t) ovat selluloosan johdannaisia, jotka ovat saaneet paljon huomiota monipuolisten fysikokemiallisten ominaisuuksiensa vuoksi. Tässä työssä testattiin eripituisilla hiiliketjuilla aminoituja kiteisiä nanoselluloosia vaahdotusprosessissa ympäristöystävällisenä vaihtoehtona laajasti käytetyille öljypohjaisille kaupallisille kerääjille. Mikrovaahdotuksia suoritettiin eri kerääjäpitoisuuksilla ja eri happamuudessa. Vaahdotuskokeet osoittivat, että aminoitu CNC muuttaa merkittävästi kvartsin pinnan vetyomisominaisuuksia ja täten joko painaa, tai vaahdottaa kvartsia. CNC:n tehokkuus riippui hiiliketjun pituudesta, ympäristön happamuudesta ja kerääjän konsentraatiosta vaahdotussysteemissä. pH 9 oli suosiollisin ympäristö niin kaupallisille kerääjille kuin nanoselluloosillekin. Heksyliamiini-CNC oli tehokkain kaikista kerääjistä, kun annokset olivat pieniä ja se ylitti 90 % saannon isommilla annoksilla. Butyyliamiini-CNC ylitti 60 % saannon ja metyyliamiini-CNC toimi painajana kaikissa tapauksissa. Kiteisten nanoselluloosien soveltuvuutta vaahdotusprosessiin pohditaan ja verrataan kaupallisiin kerääjiin.</p>			
Muita tietoja Muita tietoja: Voidaan jättää täyttämättä ellei ole mitään erityistä mainittavaa.			

# ABSTRACT FOR THESIS

University of Oulu Faculty of Technology

Degree Programme (Bachelor's Thesis, Master's Thesis) Environmental Engineering		Major Subject (Licentiate Thesis)	
Author Kimpimäki, Saku.		Thesis Supervisor Hartmann, R. M.Sc., Laitinen, O. Dr. (Tech.)	
Title of Thesis The Flotation Response of Quartz Using Aminated Cellulose Nanocrystals And Commercial Collectors			
Major Subject Fibre and Particle Engineering	Type of Thesis Bachelor's Thesis	Submission Date February 2016	Number of Pages 32 p.
Abstract <p>Since cellulose is renewable, biodegradable, non-toxic, and the most abundant natural polymeric source on earth, different micro- and nanocelluloses are considered as potential high-performance bio-based chemicals. Cellulose nanocrystals (CNCs) are cellulose derivatives that have recently gained a lot of interest due to their versatile physico-chemical properties. In this study three CNCs with different alkyl chain length were tested as collectors in quartz flotation processes as green alternatives replacing widely used oil-based commercial chemicals. Microflotation experiments were performed with varying collector dosage and pulp alkalinity. Flotation experiments proved that aminated cellulose nanocrystals change the surface wetting properties of quartz and bubbles crucially, and consequently either depress or floatate quartz. The effect of CNCs on the flotation response depended on the alkyl chain length, pH and the concentration of the collector in the flotation system. In general, pH 9 was the most favourable condition for both CNCs and commercial collectors. The flotation response increased with increasing collector concentration. Hexyl-amine-CNC was the most effective collector at low concentrations and the quartz recovery exceeded 90 % with higher dosages. Butyl-amine-CNC exceeded 60 % recovery and methyl-amine-CNC worked as depressant in all cases. The applicability of the employment of CNCs in flotation processes is discussed and compared to common commercial collectors.</p>			
Additional Information			

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ABSTRACT

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## LIST OF ABBREVIATIONS AND SYMBOLS

AP	alkoxy-propylamine
BAC	butyl-amine-cellulose
BNC	bacterial nanocellulose
CNC	cellulose nanocrystal
CNF	cellulose nanofibril
DDA	dodecylamine
EDA	ethyl-ether-amine
EDL	electrical double layer
HAC	hexyl-amine-cellulose
IEP	iso electric point
MAC	methyl-amine-cellulose
NFC	nanofibrillated cellulose
PZC	point of zero charge
TPCL	three phase contact line
P	partial pressure
c	concentration
$\gamma_i$	the surface tension of interface $i$
$\theta$	contact angle
$\zeta$	zeta-potential
$\psi_i$	electric potential of plane $i$

# 1 INTRODUCTION

Flotation is a heterocoagulation flocculation used as mineral enrichment process. It has been used in mining industry since the early 20th century for enrichment purposes of low-grade and complex ores that would have otherwise been regarded as uneconomical to be processed. Even today, froth flotation is a widely used mineral processing technique. Flotation utilises the differences in surface wetting properties of particles in order to separate the valuable mineral from the gangue minerals (Wills & Finch. 2016). For the flotation process, ores are crushed and suspended in water and the pulp is transferred to the flotation cell. The cell has an aeration system that forms air bubbles at the bottom. Mineral particles with adjusted wetting properties are attached to rising air bubbles, and subsequently lifted up to the froth which is skimmed off. Meanwhile hydrophilic minerals stay in suspension. In order to attach particles to bubbles, particles have to be rendered more hydrophobic (so called water-repellent) (Butt *et al.* 2003). At the industrial scale it is common to have several stages of flotation. (Wills & Finch. 2016).

The water consumption of flotation processes is high. Waste waters contain chemicals from flotation processes and have to be treated before transferred back into the natural water cycle. Reservoirs are often used as waste water storages and they potentially cause a major risk for the environment. Collectors are often oil-derived organic compounds. Nowadays, the industry has to minimize the energy consumption, emissions and the water consumption of the processes. Environmental friendly solutions are required in regard to the economical, ecological and social standards (Laitinen *et al.* 2014). A biodegradable collector can potentially lower the risk for the environment (Laitinen *et al.* 2016). This work compares synthesised cellulose nanocrystals (CNCs) with different alkyl chain lengths as a bio-based alternative to commercial oil-derived chemicals, i.e. ethyl-ether-amine (EDA), alkoxy-propylamine (AP), and dodecylamine (DDA). The flotation recovery of quartz is studied through bench-scale flotation experiments and the flotation recoveries of quartz using CNCs and commercial collectors are compared and discussed. Also the influence of the prevalent pH value on the recovery of quartz is investigated.

## 2 THEORY

### 2.1 Flotation

Flotation is a heterocoagulation flocculation based on varying wetting properties of different solid surfaces (Ralston *et al.* 2002). It can be divided into five microprocesses: collision, attachment, detachment, entrainment and drainage. Collisions, attachments, and detachments take place in the pulp zone and entrainment, and drainage occur between pulp and froth zone (Wills & Finch. 2016).

Collision between bubbles and particles is the first main microprocess. When the air bubble rises, the pulp flows around it and particles tend to follow the pulp. Therefore, bigger particles own a better probability to collide with an air bubble than small particle. At the same time, particles with a greater mass are less effected by the stream (Wills & Finch. 2016). The air bubble is covered with a thin water film which the particle has to penetrate to achieve an attachment. The time needed for complete penetration is called induction time and it has to be shorter than the collision time which means the time in which the particle is in contact with the bubble (particle slides down on the water-gas interface) (Ralston *et al.* 2002). Induction time can be shortened by rendering the particle's wetting properties with the help of collectors. Bigger particles have a higher velocity than smaller ones which means they have less time to penetrate the water film. This leads to a decreased attachment probability. Subsequently, an increasing particle size possesses a higher probability of particle-bubble collisions but a lower probability for orthokinetic attachments. This means that the balance between the optimum particle sizes for collision and attachment has to be taken into account (Wills & Finch. 2016). The particle sizes of minerals separated in flotation processes are usually between 10 to 100  $\mu\text{m}$  leading to a minor effect of gravity (Butt *et al.* 2003).

The surface forces between particle and bubble are repulsive van der Waals forces, the attractive hydrophobic force and the electrostatic forces (or the electrical double layer forces), which is attractive when the bubble and the particle are oppositely charged (Albijanic *et al.* 2014). Van der Waal forces are repulsive in the case of wetting films (Yoon. 2000). Hydrophobic forces are not yet completely understood (Parsons *et al.* 2011). Attractive interfacial forces between the attached particle and air bubble hast to be greater than repulsive forces effecting to obtain a good process efficiency. Forces that can



cause detachment of particles are turbulences, gravity and deceleration. According to the particles used for flotation, the optimal bubble size can be estimated. Bigger air bubbles rise with a higher speed than smaller ones. Detachment increases with increasing bubble sizes due to turbulences which may shake the particles away. Higher speed means less residence time in suspension leading to less possible effective collisions. A better option is to form a lot of small bubbles with higher specific surface area and lower velocity. This can be achieved by frothers (Wills & Finch. 2016).

Wetting can be described by the contact angle referring to the angle between solid interface and the tangent of liquid surface when the liquid-vapor interface is in contact with the solid surface. The contact angle is controlled by surface wetting properties of the materials involved. When a drop of liquid is put on the solid surface, the edge forms a defined angle. Bigger contact angle means poor wettability. If a water drop spreads over the solid surface and thus wets the surface completely, the contact angle is zero. Equilibrium state is described by relating the contact angle to the three interfacial tensions or energies, respectively, given by the Young's equation:

$$\gamma_L \cos(\theta) = \gamma_S - \gamma_{SL} \quad (1)$$

Here,  $\theta$  is the contact angle,  $\gamma_L$ ,  $\gamma_S$  and  $\gamma_{SL}$  [mN/m<sup>2</sup>] are the surface tension of the liquid, surface free energy of the solid and the solid-liquid interface, respectively. The increase of the contact angle of water can be related to an enhanced hydrophobicity which improves the flotation recovery of particles. In flotation, ortokinetic particle-bubble attachments are desired to enrich the mineral in the froth without dropping back to the pulp (Butt *et al.* 2003).

Contact angel and surface free energy studies on CNC-coated quartz pellets were conducted which showed that CNCs with increasing alkyl chain length possessed a decreasing wettability of water on the surface of quartz (Hartmann *et al.* 2016).

Bubble-particle attachment processes involves three stages: the thinning of the interfacial water film to critical thickness, the thin water film rupture, the three phase contact line (TPCL) nucleus formation, and the expansion of TPCL to form a stable wetting perimeter. Considering the attachment time, the time of TPCL nucleus formation can be excluded. The net surface forces must be attractive to complete the rupture of the water film and further expand the TPCL. The attachment time measurements can provide information

about many flotation variables such as pH and reagent type and particle type. Compared to the contact angle measurements, the attachment time gives more straight forward information about the flotation properties of minerals and with and without reagents whereas the equilibrium contact angle is a thermodynamic variable which fails to predict flotation behaviour. (Albijanic *et al.* 2010).

## **2.2 Free surface charges and the electrical double layer**

When solid particles are dispersed in water, they become either positively or negatively charged. This is caused by ionization or dissociation of surface groups, the adsorption of ions from the bulk solution, or the amorphous or crystalline structure of the mineral. Charged surfaces attract counter ions from the aqueous bulk solution. The attraction originates from the electric field of charged surface. Free surface charges and counter ions form an electrical double layer (EDL) around the solid surface. The electrical double layer describes the change of the electrical potential in the immediate vicinity of the particle's surface. It plays an important role when the properties between charged surfaces and surrounding bulk are investigated. The overlapping of the electrical double layer of similar solids which consist of identical coions provides an entropic repulsive force between particles which stabilizes them (Parsons *et al.* 2011). The general curve of the electrical potential at a charged solid surface and the different theoretical shear planes are presented in Figure 1.

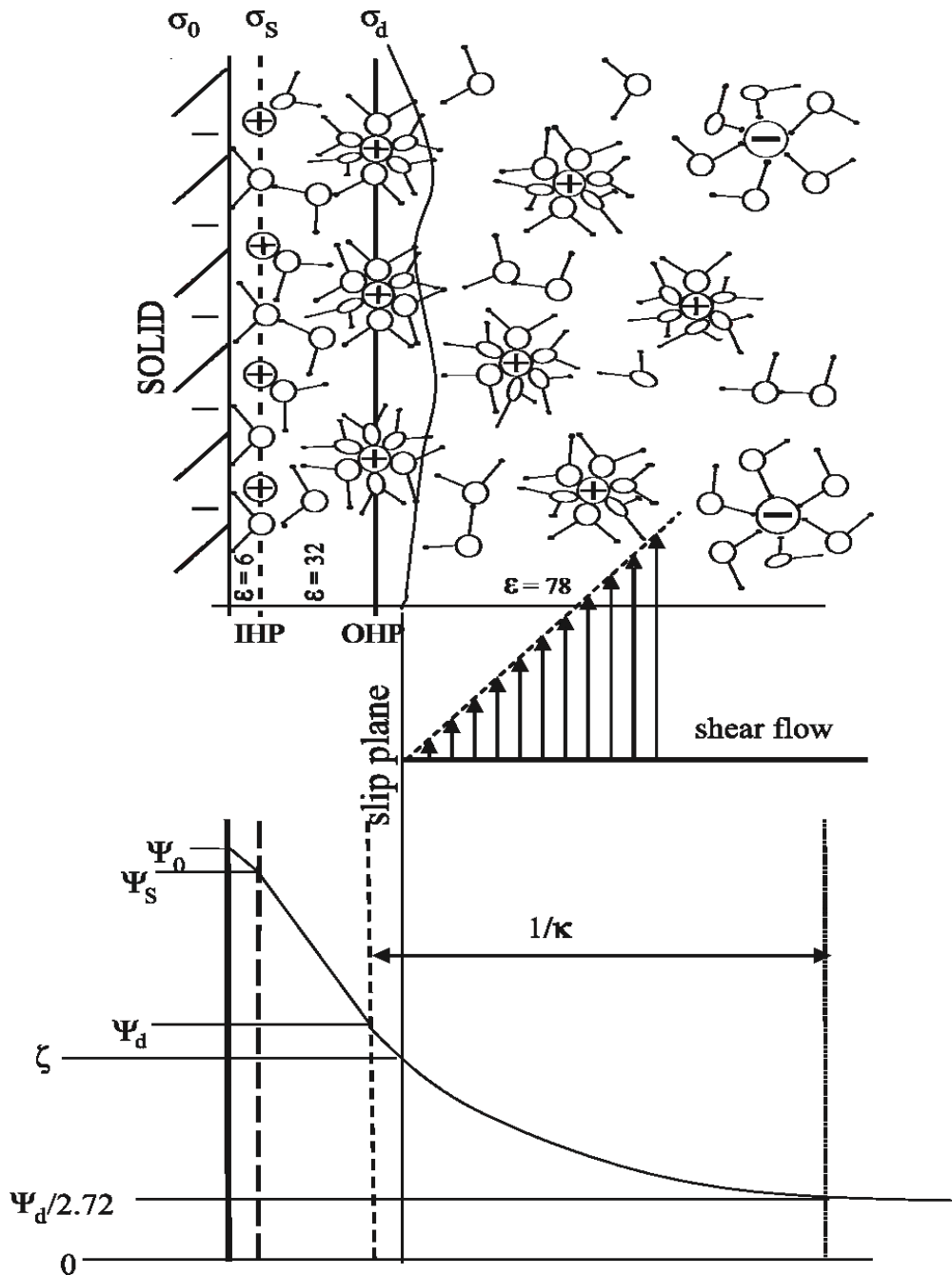


Figure 1. The Electrical double layer (Zembala. 2004).

Counter ions form an immobile or stable layer around the particle surface that is called Stern layer. The Stern layer is surrounded by the diffuse layer also known as Gouy's layer. In the diffuse layer ions are mobile (Butt *et al.* 2003).

The classical Gouy-Chapman Stern model describes the EDL structure. The electric field is changed and does change the behaviour of ions, adsorbates and solvent molecules which form the Stern layer. Electrostatic interactions determine the structure of the diffuse

layer. These interactions are described by the Gouy-Chapman theory. When no specific adsorption of ions occurs at the Stern plane the surface charge equals the electrical charge in the diffuse layer. The electric potentials in the diffuse layer can be defined using the Poisson equation and the Boltzmann law. The Poisson equation describes the relationship of the electrical potential and the electrical charge and the Boltzmann distribution determines the location of ions which are under the action of an electrical field. The potential-distance profile depends on the charge at the boundary of the Stern and diffuse layer, the dielectric permittivity and ionic strength of the solution. The geometry of the system and the boundary conditions determine the analytical solution of Poisson-Boltzmann equation and solutions are available only for simple systems. An exponential decrease of potential with the distance is predicted for flat or spherical surfaces possessing only low surface charges (Zembala. 2004).

If the solution and the surface are in relative movement, electrokinetic studies need to be applied to the Gouy-Chapman Stern model. The equilibrium of the interface can be changed also by an applied electric field. Hydrodynamic flow vanishes at a certain distance from the surface and this immobilized area is known as shear plane or slipping plane. The electrokinetic potential at the slipping plane is called zeta potential ( $\zeta$ ). There are now four potentials that can be determined, surface potential  $\psi_0$ , potential at the Stern plane  $\psi_s$ , potential at the boundary of Stern and diffuse layer (also known as outer Helmholtz plane)  $\psi_d$  and  $\zeta$  (see Figure 1).  $\Psi_d/2.718$  is a potential value determining the diffuse layer thickness (Zembala. 2004). As a result of binding one or several layers of ions or water molecules, the slipping plane is pushed further from the surface. At the distance of  $\delta$  away from the surface, molecules can move and the zeta potential is the potential at this distance from the surface (Butt *et al.* 2003). A change in  $\zeta$  refers to a charge adsorption within the Stern plane or a change in the ion concentration in solution. The ions effecting potentials are those outside the slipping plane in the diffuse layer (Fuerstenau & Pradip. 2005). When the zeta potential is zero, the so called isoelectric point (IEP) is reached and the potential determining ions have certain concentrations. This differs from the point of zero charge (PZC) in which the surface charge is zero and it describes the solid-liquid interface when the zeta potential refers to hydrodynamic interface (Butt *et al.* 2003).

## 2.3 Adsorption

Adsorption is the accumulation of a material at an interface. Adsorption is divided into physisorption and chemisorption depending on the forces causing the attraction. In physisorption intermolecular forces such as van der Waals force or hydrogen bonding occurs. In chemisorption, a chemical reaction takes place, e.g the formation of covalent bonds. Atoms, ions and molecules are called adsorbate when attracted on the adsorbent meaning a liquid or solid surface. When not yet attracted on adsorbent the substances are called adsorpt. The most important parameter involved in adsorption is the partial pressure  $P$  for the adsorption of gases and concentration  $c$  for the adsorption of liquids on solids (Butt *et al.* 2003). Adsorption is based on dispersive interactions (van der Waals interactions) and polar interactions (such as electrostatic interactions) (Parsons *et al.* 2011). The adsorption of collector molecules changes the particle surface wetting properties to either more hydrophobic or hydrophilic to achieve enrichment in the foam or the stabilization of the interfacial water film. The alkyl chain length of the collector molecule has several effects on the system. In flotation, collectors adsorb on the mineral surface with the polar functional group and the non-polar alkyl chain group is orientated to the liquid (Wilss & Finch. 2016).

The EDL at the solid/liquid interface controls the adsorption of collectors on mineral surface. Particles and collector molecules are usually oppositely charged in systems where adsorption based on physisorption are considered. Chemisorption takes place even when collectors and minerals surfaces have identical charges. The pH value of the system effects the adsorption crucially. Cationic collectors lose their adsorption sites to hydrogen ions at low pH and hydroxides and anions limit adsorption of anionic collectors at high pH (Albjanic *et al.* 2010). Contrary, the degree of protonation is higher at low pH values in case of cationic collectors and this enhances the electrostatic interactions between the negatively charged mineral surfaces and positively charged ammonium ions. Hydrogen bonding between ammonium ion and silanol group of the mineral allows further precipitation of neutral amines on the surface. Consequently the ratio between neutral and protonated amines effects the adsorption density on the surface (Vidyadhar *et al.* 2002). The point of zero charge is an important property of the mineral. The PZC is often described as the pH value where the net charge of the mineral free surface is zero. At the pH values below the PZC, minerals can only be floated with anionic collectors because the positive surface charges are present at the surface. Consequently, particles bear

negative charges when pH value is above PZC and cationic collectors are used. The zeta potential is a proper way to describe and predict interactions between mineral particles and collector molecules (Fuerstenau & Pradip. 2004). Collector molecules can bind as layer or layers on the mineral surface “pushing” the shear plane further away from the mineral surface.

To achieve tailored hydrophobicity of the mineral surfaces, flotation reagents, called collectors, need to be applied. Collector molecules adsorb selectively on the mineral surfaces changing particle’s surface wettability. Further flotation reagents are frothers and regulators. The frother is used to form and maintain an optimum and stable gas bubble size and froth. Regulators can activate or depress the adsorption of collectors leading to particle-bubble attachment or regulators are used to control the pH value of the system (Wills & Finch. 2016).

Collectors are soluble amphiphilic molecules (amphiphiles) also known as surfactants. Amphiphiles consist of a hydrophilic and a hydrophobic part (Butt *et al.* 2003). Collectors are used to selectively modify surface wetting properties of the mineral by increasing the hydrophobicity of particles via adsorption. Collectors can be classified into two main groups: non-ionising and ionising collectors and ionising collectors can be further divided into two classes by the type of ion; anionic and cationic collectors. In this work we will focus on cationic collectors which are used to float silicates, oxides, carbonates and alkali earth metals. The effect of cationic collectors originates from the behaviour of the pentavalent nitrogen. The amines are most commonly used. Cationic collectors physisorb through electrostatic attraction of the polar head and the opposite surface charges of the solids. The hydrophilic polar head group is in contact with the solid surface and the hydrocarbon chain is orientated to the bulk causing the change of the wetting property. The hydrophobicity of different alkyl groups and hydrophilicity of the amine group determines the adsorption and wetting properties of the collector (Wills & Finch. 2016).

If the concentration of the collector is too high in pulp, this causes the flotation of unwanted minerals and forms poly-layers on valuable particles so that the number of hydrocarbons orientated to water is reduced. Thus, the hydrophobicity of valuable particles is decreased leading to a low flotation efficiency. Instead of increasing the collector concentration of the solution, the properties of collector molecules can be changed. Hydrocarbon chain length and chain structure effects the adsorption and

solubility of collectors. For this, molecules with longer hydrocarbon chain lead to a higher flotation response of the particles but simultaneously lowers the solubility of collector. Chains with branches own better solubility than straight ones (Wills & Finch. 2006).

## **3 MATERIALS AND METHODS**

### **3.1 Quartz**

Minerals are characterised by the polarity of their surfaces. Covalent molecules hold together by van der Waal forces as non-polar minerals and they are naturally hydrophobic. Polar minerals are held together by strong covalent or ionic bondings. Polar minerals can be further divided into five groups, groups 1 includes minerals with low polarity on the surface and group 5 the most polar ones. As the magnitude of polarity rises so does the surface reactivity with water molecules leading to increasing hydrophilicity. Quartz belongs to group 5 and thus the surface has to be rendered hydrophobic for flotation. Quartz, being a strongly polar mineral due to its strong covalent bonds and possessing high surface free energy values, is naturally hydrophilic at natural pH range (Wills & Finch. 2016).

Quartz, delivered by Sibelco from the deposit of Nilsjä, Finland, was grinded in a grinding mill (Retsch PM 200) with 7 iron balls per grinding cell with grinding time of 3 minutes and grinding speed of 300 rpm. The grinded quartz was sieved to achieve a size fraction between 63 and 125  $\mu\text{m}$ .

### **3.2 Cellulose nanocrystals as collector molecules**

Cellulose is the most abundant natural polymeric source on earth and has several promising properties to be used in mineral processes; such as high aspect ratio, very high specific surface area and versatile chemical compositions. Cellulose is biodegradable, low-toxic and renewable. Cellulose's raw materials are plants, bacteria and tunicates (Siqueira *et al.* 2010).

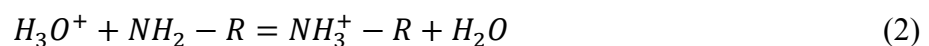
Nanocelluloses are synthesised from lignocellulosic-based materials. Natural fibres consist mostly of cellulose, lignin and hemicellulose and small amounts of pigments and extractives. The chemical structures of these cellulosic fibres are complicated. Glucose units are connected repeatedly forming a cellulose polymer, which possesses properties that are essential for semicrystalline fibre morphologies formed by extensive hydrogen bond networks (Siqueira *et al.* 2010). Nanocelluloses are characterised by their synthesis routes, dimension, and functionality to cellulose nanofibrils (CNF), cellulose



nanocrystals (CNC) and bacterial nanocellulose (BNC). Cellulose nanocrystals, also known as nano whiskers are 2-20 nm in diameter and 100-600 nm in length (Khalil *et al.* 2014).

In this study, methylamine-CNC (MAC), butylamine-CNC (BAC) and hexylamine-CNC are tested as collectors. These modified CNCs were synthesised from bleached kraft hardwood (*Betula pendula*) pulp using consequent periodate oxidation and reductive amination reactions. Morphological dimensions of all aminated CNCs are similar for all alkyl chain lengths but the extension of the chain length increases the affinity between nanocrystals (Hartmann *et al.* 2016). The addition of hydrophobic alkyl-amino groups to the CNC structure leads to the amphiphilic behaviour of CNCs. The back bone of cellulose is hydrophilic (Visanko *et al.* 2014). There have been contact angle and surface free energy studies on CNC-coated quartz pellets which showed that CNCs, with increasing alkyl chain length, possessed an enhancing water repelling effect on the quartz surfaces (Hartmann *et al.* 2016).

Quartz, having oxygen on its surface, can be easily protonated and further deprotonated by hydroxyl groups (OH) of the solution. Thus, the pH value of the solution affects significantly the properties of interfaces. For example, the protonation of CNCs amine group in acidic solution follows the reaction:



where R is the hydrocarbon chain of a amine group. Therefore, the number of protonated amine groups is dependent on the pH value and thus the concentration of oxonium ions in solution (Hartmann *et al.* 2016).

Electrostatic interactions between CNCs and quartz occur when the species possess opposite free surface charges. Due to opposite charges, the adsorption of CNCs on quartz is possible. There have been studies on adsorption phenomena of aminated cellulose nanocrystals on quartz. Hartmann *et al.* (2016) studied interactions between CNCs and quartz using amines with three different alkyl chain lengths: methyl amine (MAC), butyl amine (BAC) and hexyl amine (HAC). The polyelectrolyte titration of suspended CNCs and quartz in water showed that quartz bear slightly negative surface charges and CNCs

had positive charges under neutral and acidic conditions (pH-values 3-9). The specific surface charges of CNCs decreased with increasing pH value. HAC had the highest surface charge at pH of 5 but also strongest descent with rising pH-value reaching the PZC at pH 9. The protonation was observed mostly at pH 5. Mixtures of quartz and CNCs were used to study the adsorption of CNCs on quartz. In general, an increase of the alkyl chain length was found to be restrictive for the protonation of amine groups (Hartmann *et al.* 2016).

The pH value of solution has a substantially effect on adsorption phenomena of CNCs on quartz. All CNCs adsorbed most effectively at pH 9. The alkyl chain length correlated to the mass of adsorbed CNCs where the longest one had the strongest interactions with quartz. At low pH range, CNCs had very high surface charges compared to quartz limiting the interactions between the species. Also repulsive forces between CNCs are much higher when the number of free surface charges is higher: adsorbed CNCs were hypothesised to form an electrostatic barrier that blocks other CNCs from the surface. The mass of adsorbed CNCs was inversely proportional to the degree of protonation which proved the important effect of surface charges of CNCs on the adsorption on quartz (Hartmann *et al.* 2016).

### **3.3 Ethyl-ether-amine (EDA)**

EDA is an alkyl ether monoamine used for the flotation of quartz. Ether amines are one of the most used collectors in reverse cationic flotation plant practice. Ether mono-amines are more effective than ether di-amines even though di-amine has an extra polar group. Ether mono and di-amines are often used as combinations to achieve maximum recovery and selectivity. Ether amines play also the role of a frother effecting bubbles and froth (Araujo *et al.* 2005). The degree of neutralisation of ether is an important parameter. It is a molar ratio between amine and acetic acid used to neutralise ether amine to make it more soluble. But when the amine content is lower, the hydrophobic and frothing abilities of the collector are decreased (Filippov *et al.* 2014). The optimum quartz recovery in flotation experiments was between pH 8 to 10 (Laitinen *et al.* 2014), according to Vieira and Peres (2007) pH 9 was the most favourable.

### 3.4 Dodecylamine (DDA)

DDA is a collector that is used in reverse cationic flotation to separate quartz and silicates from ferrous or magnetic ores. At low pH values, adsorption occurs due to coulombic attractions which means that ions of amines adsorb as an individual ion on the quartz surface. Higher pH value allows a better coverage of ions until the solubility rate starts to be a limiting factor. (Pugh *et al.* 1996). Quartz recovery is over 90 % with concentration of  $5 \cdot 10^{-5} \text{ mol/l}$  at pH values between 7 and 8 (Yang *et al.* 2014).

### 3.5 Alkoxy-propylamine (AP)

Alkoxy-propylamine has been used as collector in flotation of the aluminosilicate minerals. Alkoxy-propylamines have two polar groups,  $-\text{NH}_3$  and C-O-C, activating adsorption and thus poses stronger electrostatic interactions with aluminium silicate minerals than dodecylamines. The effect of the C-O-C-group increases with increasing pH-value but when pH is higher than 7, the efficiency of cationic collector decreases and the change of the  $\zeta$ -potential is smaller (Cao *et al.* 2004).

### 3.6 Microflotation

For each flotation experiment, 5.0 g of quartz were weighted into a 250 ml beaker and 150 ml of deionised water was added. The solution was continuously mixed with a magnetic stirrer while adjusting the pH and adding the reagents. A 0.1 M and 1.0 M NaOH and HCl solution were used to adjust the pH and after the adjustment, the suspension was stirred for 5 min before adding a certain amount of collector. CNC collectors were treated in ultrasound bath for 3 min to re-disperse possible agglomerates and transferred to the suspension. The conditioning time was 5 min and subsequently, 35  $\mu\text{l}$  of Dowfroth frother was added and stirred for 1 min.

Microflotation was performed in a 400 ml cell connected to a peristaltic pump providing the circulation of the suspension through the system. The pump speed was 1400 ml/min and the airflow was 25 ml/min. First, the cell was filled with deionised water over the suspension circulation input. Then the sample was added and the cell filled with deionised water to the desired level. Finally, the air flow was introduced. The flotation time was 20 min per experiment. The over- and underflows were recovered and vacuum-filtrated

trough filtration papers into the Büchner funnel. Samples were then dried and weighted. All the filter papers were weighted and marked before using.

CNCs were provided by the institute. Each CNC solution was added to the suspension representing a concentration of 0.1; 0.2; 0.5; 1.0; 2.0 and 3.0 g/kg based on the total mass of quartz. Each dosage of each collector was flotated at pH 5, 7, and 9. A reference flotation containing no reagents was performed at all three pH values.

## 4 RESULTS AND DISCUSSION

The flotation of pure quartz using only the frother lead to a recovery of quartz about 13 % over the whole pH range. In Figure 2, the flotation recovery of quartz using CNCs is presented. According to Figure 2, MAC acted as depressant, and for all experiments, the flotation recovery was smaller than without flotation reagents. There can be seen a small decrease in the recovery when the pH is increased from 5 to 7 but when pH 9 is reached recovery is approximately the same as at pH 5.

BAC showed an enhancing recovery with increasing pH at small concentrations. With higher concentrations the trend was opposite: BACs highest flotation response was observed in an acidic solution and an increasing pH value reduced the recovery. The most interesting point, in case of BAC, is that almost the same recovery was reached with a ten times smaller dosage in alkaline solution referring that BAC is most efficient in alkaline environment. Nevertheless, 60 % recovery was reached only with the biggest dosage 3.0 g/kg. BAC clearly reduces the induction time of the particle-bubble attachment and promotes flotation response of quartz as seen in Figure 2.

HAC, having the longest alkyl chain, was clearly the best CNC-collector exceeding 60 % recovery with all dosages (at pH 9). At the smallest and the biggest dosage, the recovery increased with increasing pH value. With dosages of 0.2 g/kg and 0.5 g/kg, the trend was not as clear as it was with other dosages. Dosage of 1.0 g/kg gave almost the same recovery at all pH values. With dosage of 2.0 g/kg, a small increase of the recovery was found with increasing pH but at 3.0 g/kg, there was a clear ascent between pH 5 and 7 and minor increase when pH was 9. There was no significant change in flotation response after the dosage of 1.0 g/kg. The flotation response of HAC, presented in Figure 2, indicated that HAC successfully worked as a collector molecule and shortened the induction time of quartz particles rupturing wetting film of air bubbles. Kowalczyk (2015) studied hexyl-amine as an example of a short chain amine as a reagent in flotation and proposed that hexyl amine plays a role of a frother. However, flotation response studies of this work showed that when attached to the hydrophilic cellulose backbone, hexyl-amine does work as a collector.

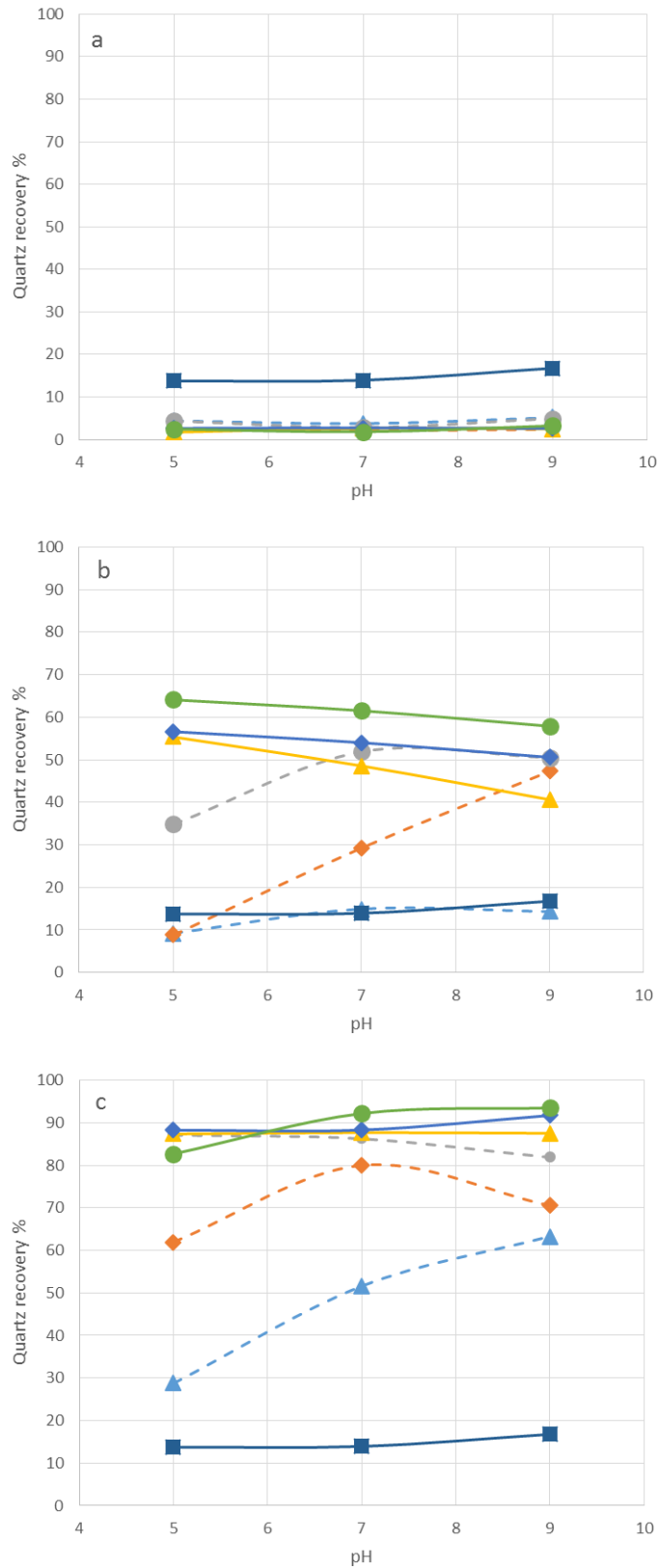


Figure 2. Flotation recovery of quartz with CNCs as collectors: (a) MAC, (b) BAC and (c) HAC. Dosages are marked as ● for 0.5 and 3.0 g/kg, ◆ for 0.2 and 2.0 g/kg, ▲ for 0.1 and 1.0 g/kg. Three smallest dosages are drawn with dashed lines and reference response is marked by ■.

In Figure 3, the flotation response employing commercial collectors is depicted. Therefore, EDA showed almost linear decrease in recovery with increasing pH when dosages were small. With dosages 1.0 g/kg, 2.0 g/kg and 3.0 g/kg recovery was over 95 % at pH 7 and 9. In acidic solution recovery was at the smallest but still around 90 %.

Almost 100 % recovery was reached with three biggest dosages of APA at the pH of 9. The smallest concentration of collector showed minor improvement in recovery but the dosage of 0.2 g/kg exhibited an increase of the flotation recovery about 20 % between pH 5 and 9. With higher dosages the change in recovery was smaller between different pH values but the trend was same excluding dosage of 0.5 g/kg where the best recovery was observed at pH 7. It must be mentioned that with the three biggest concentrations, the recovery is smaller with bigger dosage of collector. This may be explained by bi- or multilayer formation on quartz surface caused by too high collector concentration: carbon chains of additional collector molecules (adsorpts) interact with adsorbates so that the polar heads of additional collectors are orientated to liquid reducing the effect of collectors (Albijanic *et al.* 2014).

The smallest dosage of DDA showed a decreasing recovery with increasing pH but when the dosage is doubled to 0.2 g/kg, the collector behaves vice versa. The increase of the collector concentration improved the flotation performance. Dosage 2.0 g/kg was the exception giving the poorest result at the pH 7 and the best at 9.

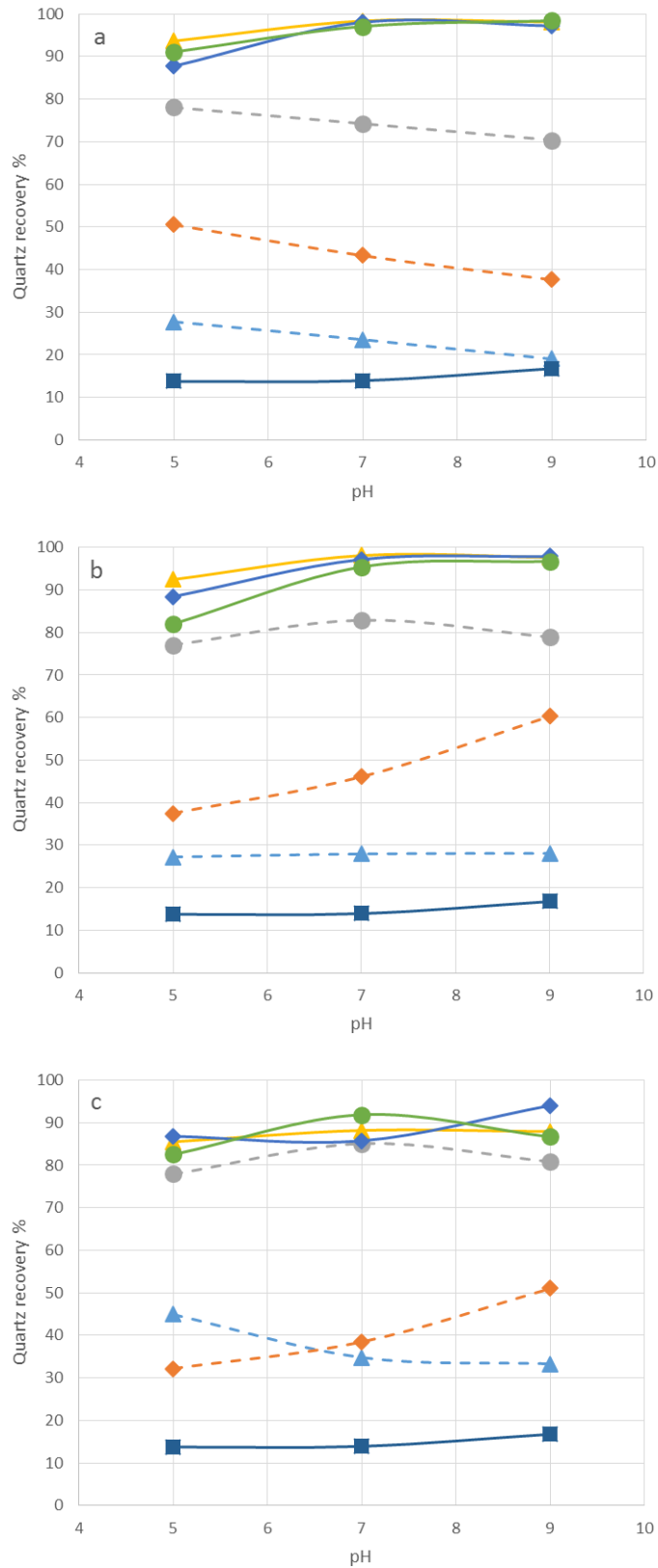


Figure 3. Flotation recovery of quartz with commercial collectors: (a) EDA, (b) AP, and (c) DDA. Dosages are marked as ● for 0.5 and 3.0 g/kg, ◆ for 0.2 and 2.0 g/kg, ▲ for 0.1 and 1.0 g/kg. Three smallest dosages are drawn with dashed lines and reference response is marked by ■.



Extended alkyl chain length indicates better collecting efficiency in the case of CNCs. Hexyl-amine has the best recovery in all cases both in acidic and alkaline environment. Both butyl-amine and methyl-amine hindered the recovery when the dosage was 0.1 g/kg with an exception of pH 7 in case of BAC. BAC works as depressant also with the dosage of 0.2 g/kg at pH 5 but otherwise it enhances quartz recovery. The mass of adsorbed CNCs increases with increasing pH meanwhile the specific surface charge decreases and HAC reaches PZC at pH 9. At low pH values CNCs bear high specific surface charges and thus the repulsive forces between CNCs are strong. CNCs may form an electrostatic barrier on the quartz surface that prevents further adsorption. Consequently, increased pH lowers specific surface charges of CNCs and CNC-CNC interactions are reduced allowing more CNC-quartz interactions. Also attractive interactions between CNCs and water molecules are reduced due less free surface charges and the agglomeration of CNC coated quartz particles is enhanced when repulsive forces between CNCs are attenuated. Agglomerates have better collision probability but also a shorter time of attachment. In contrast, agglomerates possess greater mass than individual particles and are thus more effected by gravity and if gravity exceeds attractive interfacial forces particles detach air bubbles. This may explain why HAC reaches its maximum recovery when the dosage is 1.0 g/kg at pH 7 and 9. When the dosage is bigger recovery is smaller at these pH values but at pH 5, the recovery is enhanced. At pH 5 the specific surface charge is still high and thus there are less agglomerates. The standard free energy of protonation being positive for all CNCs at pH 9 means that the number of deprotonated amine groups is higher than the number of protonated ones (Hartmann *et al.* 2016).

HAC and BAC are as good as commercial collectors when used in small doses and HAC was similar with AP and EDA at high doses. Interestingly, HAC was the most effective collector with three smallest dosages. Therefore, the flotation recoveries of HAC and commercial collectors at a concentration of 0.2 g/kg are compared in Figure 4.

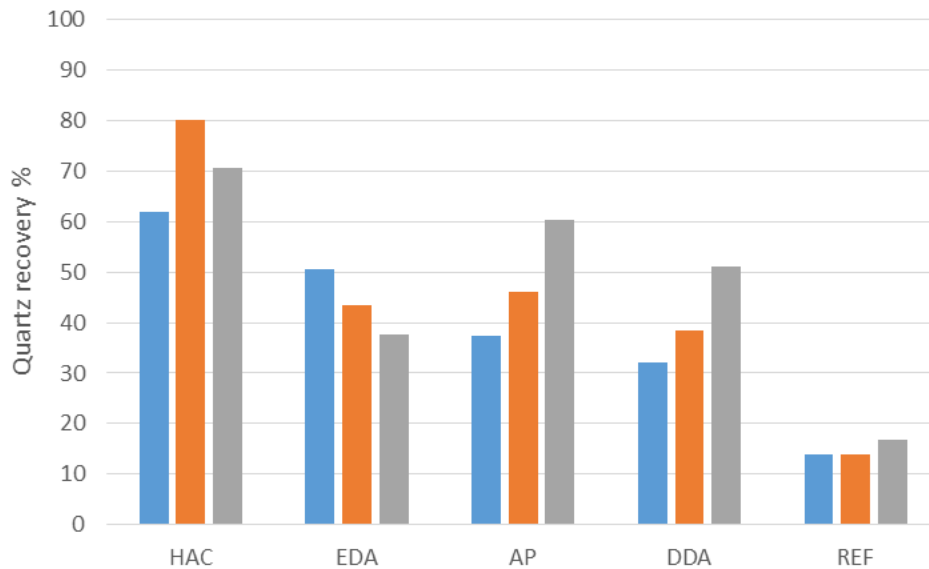


Figure 4. Flotation recovery of quartz with collector dosage of 0.2 g/kg. Bars present pH values of 5, 7 and 9 from left to right.

An Individual CNC is roughly 80-150 nm long and carries multiple alkyl amine groups. At low pH values high amount of amines are protonated to alkyl-ammonium ions and individual molecules bearing many free surface charges repelling each other. Consequently CNCs adsorb on the mineral surface, however, most parts of the molecule remain hydrated and its structure is orientated to the liquid. Finally, the charged molecules, repelling each other, form an electrical barrier on the quartz surface which prevents further CNCs to adsorb. At high pH, the degree of protonation is decreased and thus the specific surface charge of CNC is smaller which leads to the formation of poly-layers of CNCs on the particle surface enhancing the particle's surface hydrophobicity. CNC adsorbing laterally to poly-layers may cover high surface energy sites of a particle such as corners and edges and thus reduce the induction time. MAC has relatively high specific surface charge over the whole pH range and thus polylayers may not occur (Hartmann *et al.* 2016). Electrostatic repulsion between CNCs in the adsorption layer could be reduced using non-ionic surfactant molecules as co-adsorbents, such as alcohols, and thus flotation at low pH values would be more effective (Filippov *et al.* 2010).

In comparison commercial collectors are roughly 1-10 nm long and an individual molecule has only one amine group (monoamines) and alkyl chain (Oliver *et al.* 2013). Molecules adsorb when amine groups are protonated and optimum flotation should occur at low pHs value. The more adsorbed molecules, the more hydrophobic alkyl chains

directed to liquid phase. At low pH range AP's functional group C-O-C combines with  $H^+$  and loses its adsorption power. When pH exceeds 7 the number of cations is reduced and further increase of pH has no effect (Cao *et al.* 2004). This may explain the behaviour of EDA and AP.

## 5 SUMMARY

Aminated cellulose nanocrystals with three different alkyl chain lengths were tested as collector molecules and compared with commercial collectors. Microflotation experiments of quartz were performed at pH values 5, 7 and 9 for six different dosages of each collector. The effect of alkyl chain length and concentration of collectors, and the effect of pH of the pulp were studied. First, the increasing alkyl chain length of CNCs indicated a better flotation response. MAC worked as depressant in all cases and no significant change in flotation response were observed with varying dosages. BAC reached the maximum recovery of 64 % and the recovery with HAC exceeded 90 %. All of the commercial collectors exceeded 90 % recovery. EDA was the most effective commercial collector.

Both, CNCs and commercial collectors showed enhanced flotation recovery with increased concentration, with the exception of MAC. HAC was clearly the best collector of all at small dosages reaching almost its maximum flotation recovery already at the dosage of 0.2 g/kg and no significant change in recovery were observed with bigger dosages. The dosage of 0.2 g/kg seems to be enough to form mono-layers covering high surface energy areas and additional CNC on the surface has only a minor effect.

Microflotation experiments indicated that BAC and HAC act as collector at the whole pH range from 5 to 9. The pH 9 was observed to be the most favour for HAC almost in all cases and for BAC at small dosages. The effect of pH in case of MAC was negligible compared to others, but at pH 7 quartz were depressed for the most. The recovery of quartz was increased with more alkaline pH in cases of EDA and AP, especially at big dosages. The trend was just the opposite pH 5 being the optimum for EDA at small dosages. DDA was effective at the pH 7 in average and big dosages. The recovery dependency on the pH was found to decrease with increasing dosage.

Both, BAC and HAC performed efficiently at small concentrations and HAC was nearly as good as commercial collectors at high concentrations, proving that bio-based, environmentally-friendly CNCs are effective alternatives for oil-based commercial collectors. The fact that CNCs reached higher recoveries at low concentrations than the commercial collectors is a fundamental observation. Especially interesting is that HAC is more efficient than DDA although DDA has four more methyl-groups in its structure than

HAC. In future, the selectivity, the behaviour of CNCs in mixtures and the effect of background salt solutions has to be studied to proof the applicability in industrial scale. For example, MACs behaviour as depressant throughout the whole pH range offers an interesting opportunity to study CNCs as flotation reagent mixtures, where MAC and HAC would depress and flotata different minerals selectively. Electrokinetic studies need to be performed to get a better picture of CNCs interactions at the hydrodynamic interfaces and thus illuminate the adsorption phenomenon of CNCs on solid surfaces.

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