NANO-ENTITIES FOR SURFACE MODIFICATION OF MINERALS. IMPLICATIONS FOR FLOTATION

Authors: Bertil I. Pålsson[a*], Tommy Karlkvist[a], and Aji P. Mathew[b]
a/ Minerals and Metallurgical Engineering (MiMeR), Luleå University of Technology, Sweden
b/ Department of Materials Science and Mathematics, Luleå University of Technology, Sweden
*/ Corresponding author: bertil.palsson@ltu.se

ABSTRACT
Adsorption of nano-entities (nano-cellulose and nano-chitin) on quartz and magnetite was investigated as a function of pH with measurement of Zeta potential as a tool. The results show strong adsorption of the nano-entities on both minerals, leading to charge reversal. However, the adsorption appears to be largely non-preferential over the concentration and pH ranges investigated.

Micro-flotation results show that both nano-entities float quartz to the same extent, and that the same is true for magnetite. However, the amount floated is higher for quartz. There is also an indication that nano-chitin at pH 8 has some preference for quartz over magnetite.

Mini-flotation results for mineral mixtures at pH 8 with nano-chitin and flotation reagents show that nano-chitin can selectively float quartz for the given conditions, but the recovery is low. If oleate is added, the selectivity is lost. This means that the nano-entity is probably not a cationic activator, rather it induces some little hydrophobicity to the quartz surface on its own.

1 INTRODUCTION

Originally, an idea from Luossavaara-Kirunavaara AB (LKAB), Minerals and Metallurgical Engineering (MiMeR) at LTU has done tests to investigate whether nano-entities will adsorb on minerals. The minerals of interest for this study are magnetite and quartz, since they represent an interesting mineral pair from a beneficiation point of view. The nano-cellulose (named CNC_{BE} or CNC) and nano-chitin (named ChNC or Chitin) used for the studies were produced by the Department of Material Science and Mathematics, at LTU

The main reason for testing nano-entities is that in production of magnetite concentrates for pellet fines, the silicon content is a major quality concern. Silicon may be present as quartz, dark iron-containing silicates or as mixed particles with magnetite. The traditional method to remove siliceous gangue from magnetite pulps is to float it with amine collectors. However, the use of amines in flotation has raised environmental concerns, since most amines show toxicity towards aquatic life. Therefore, the mining industry wish for an alternative to amine collectors that will not have the same amine activity in the pulp liquid phase and by that also shows much reduced free amine levels in the effluents from tailings ponds.

It is known from the literature that nano-cellulose has shown some flotation and/or depression action of hematite and quartz (Laitinen et al., 2014) and aluminium oxide and quartz (Laitinen et al., 2016). These studies have been done on single mineral systems, and in microflotation cells. The same author group have also described the production of amine-modified cellulose nano-crystals (Sirviö et al., 2016).

The general methodology for studying mineral matters of relevance for the magnetite-silicate system with adsorption and micro-flotation is described by Karlkvist, et al. (2015). The project presented here was executed in the following steps:

1. Production and characterisation of different nano-celluloses and nano-chitins with different surface groups.
2. Adsorption studies of select nano-celluloses and nano-chitins on magnetite and quartz to establish best conditions for charge reversal of mineral surfaces. This was done over a wide pH range.
3. For the best combinations of nano-cellulose/nano-chitin, mineral and addition rate, micro-flotation studies on single minerals were carried out. In a first stage the influence of the nano-entities themselves was checked.
4. In a later stage, the micro-flotation was augmented by a small addition of a weak frother to check whether nano-cellulose and/or nano-chitin adsorption might lead to slightly hydrophobic mineral surfaces.
5. A further stage was to check whether a traditional collector molecule (oleate) with opposite charge to the modified mineral surfaces floats the quartz. When this is achieved by inorganic cations, it is called cationic activation of mineral surfaces and a similar mechanism might be possible after adsorption of nano-entities.
6. A final stage was to try with mixtures of magnetite and quartz in the micro-flotation cell to check for any possible selectivity between the minerals.
7. Mini-flotation with mixture of magnetite and quartz was used for a few selected conditions. Since this is a binary mineral mixture, the product qualities were established by a He-pycnometer, and proper product balances cold be calculated.

2 MATERIALS AND METHODS

2.1 Production of nano-entities

2.1.1 General

Cellulose from wood prepared from the bioethanol processing route was used as the raw material for cellulose nano-crystals. Pure cellulose was supplied by SP Processum, Örnsköldsvik, Sweden, as water suspensions of 17 wt-%. Crab shell residue purchased from Sigma Aldrich GmbH (Germany) was used as the raw material for the preparation of chitin nano-crystals. All other chemicals used, like H_2SO_4 (96%), NaOH, HCl (37%), KOH, are of reagent grade and were purchased from VWR (Sweden) and used as received.

2.1.2 Nano-cellulose

Nano-cellulose was produced from cellulose nano-crystals from a bioethanol process (Mathew et al., 2014). Cellulose was extracted from un-barked wood by a dilute acid hydrolysis using a bioethanol process, The purified cellulose (17 wt-% suspensions) obtained after acid hydrolysis in a bioethanol process plant and a refining process was diluted into 1.5 wt-% suspensions, mixed by shear mixture and passed through the homogenizer, 10 times to obtain a thick gel of nano-cellulose (CNC_{BE}) (Mathew et al., 2014). The flow chart of the various steps used for the isolation of CNC_{BE} is given below (Fig. 1). The homogenization process has been performed using a lab scale homogenizer. The yield of isolated CNC_{BE} was 100 %.

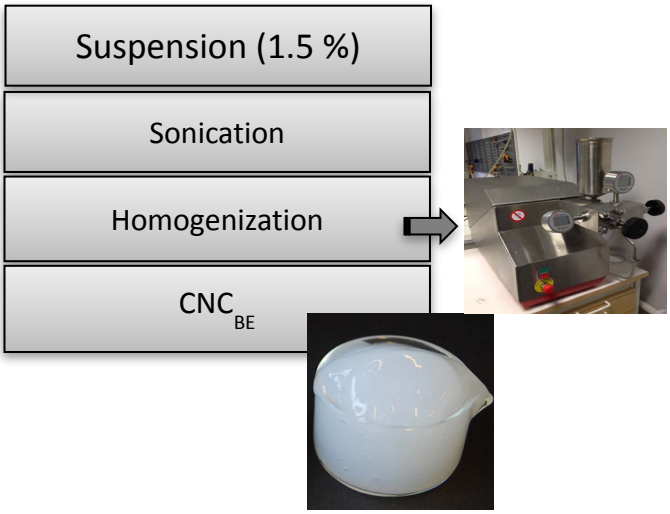


Figure 1. Steps for the isolation of CNC_{BE}

The amount of CNC_{BE} initially produced was calculated to be 60 g (dry weight) and was used adsorption and flotation studies.

2.1.3 Nano-chitin

Nano-chitin came from chitin nano-crystals from crab shell (ChNC); Crab shell chitin was purified using alkali treatment followed by chlorite bleaching to remove proteinatious matter and other components in crab shell and obtain refined chitin. Chitin whiskers suspension was prepared by hydrolysing the purified chitin sample with 3 M HCl at the boil for 90 min under stirring (Nair, et al., 2003). The ratio of 3 M HCl to chitin was 30 cm^3/g. After acid hydrolysis, the suspension was diluted with distilled water followed by centrifugation (6000 rpm for 15 min). This process was repeated three times. Next, the suspension was transferred to a dialysis bag to soak in distilled water for one week with the distilled water changed every day. The dispersion of whiskers was completed by a further 5-min ultrasonic treatment for every 30 cm^3 aliquot. It was subsequently stored at 6 °C after adding sodium azoture to avoid bacterial growth until use. The various steps for the isolation of nano-chitin is summarized in Fig. 2.

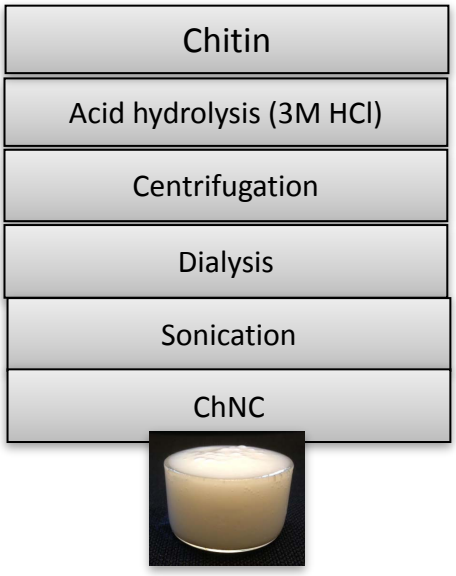


Figure 2. Steps for the isolation of ChNC

The quantity of ChNC isolated by the process was determined using thermogravimetric analysis and was calculated to be 10 g (dry weight). About 5 g was for initial adsorption studies.

The zeta potentials of the produced nano-entities, at different pH, were measured using a Zeta sizer nano ZS, Malvern (UK) at 25 °C. The concentrations of all measured samples remain the same at 0.05 wt-%. Sample viscosities were detected by a vibro-viscometer (SV-10), Japan, and used as key parameter for zeta potential measurement.

Surface charge content including carboxylate, amino and any other groups was determined by electric conductivity titration or spectroscopy methods.

2.2 Quartz

A sample of 1 kg high-purity quartz was available at MiMeR. It had been bought from Gregory, Bottley & Lloyd Ltd., United Kingdom. The sample was crushed in a Retsch laboratory jaw crusher BB3 to <3 mm. Thereafter, it was treated with a hand magnet to remove residual iron. The non-magnetic part was ground in a dry laboratory stainless steel rod mill Ø8”x13” to 50 per cent by mass less than 100 µm, cf. Fig. 3. Then, the ground product was first wet-sieved on a stack with 38, 75 and 150 µm sieves. The size fraction <38 µm was further sieved in an ultra-sonic bath on a 5 µm polymer sieve (Nybolt PA-5/1). The procedure gave 80 g <5 µm dry quartz powder to be used for measurements of Zeta potential.

The size fractions 38-150 µm were combined and used in the flotation studies.

2.3 Magnetite

The magnetite was produced from samples of MEFCON provided by LKAB/MetLab. It was very fine from the beginning, d_{90} 31 µm, so it was not ground, cf. Fig. 3. It was wet-sieved on the same sieve stack as for quartz. In addition, it was also sieved on a 20 µm wire-mesh sieve and the 5 µm polymer sieve. This resulted in approx. 250 g of dry magnetite powder <5 µm to be used for measurements of Zeta potential.

Additional samples of MEFCON provided by LKAB/Kiruna were used to produce the 38-150 µm fraction for the flotation studies.

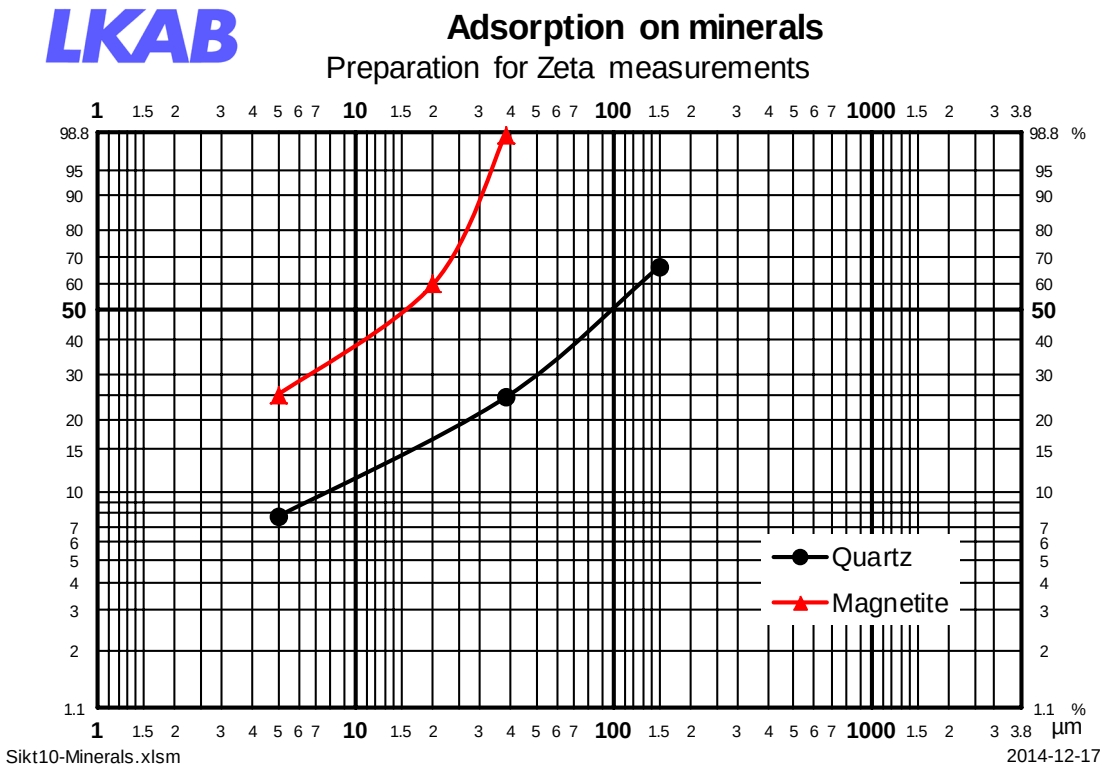


Figure 3. Particle size distributions for the minerals produced

2.4 Flotation reagents

Adjustment of pH was done with NaOH and HCl. Both technical grade.

The collector was sodium oleate (Avantor Performance Materials), and the frother 4-methyl-2-pentanol (MIBC) of technical grade.

2.5 Zeta potential

Zeta potential measurements were done using a ZetaCompact (CAD instruments) instrument. A background electrolyte $1 \cdot 10^{-3}$ M NaCl was used and the solid concentration of the samples was 0.50 g/L. Adjustments of pH with NaOH and HCl. Each sample was equilibrated for 10 minutes on a laboratory shaker. The results were calculated using the Zeta4 software® with the Smoluchowski equation and are an average of five repeated measurements (each time with different aliquots) on the same sample.

In Figure 7 and onwards, the marker show the average of the measurements in a specific point. The error bars shows the average of the standard deviations from the individual runs. In the measurements with nano-cellulose these become very large, but this seem to be related to the nano-particles themselves, or clusters of them, also being detected, thus making the electrophoretic mobility distributions very wide or even bimodal, cf. Fig. 4.

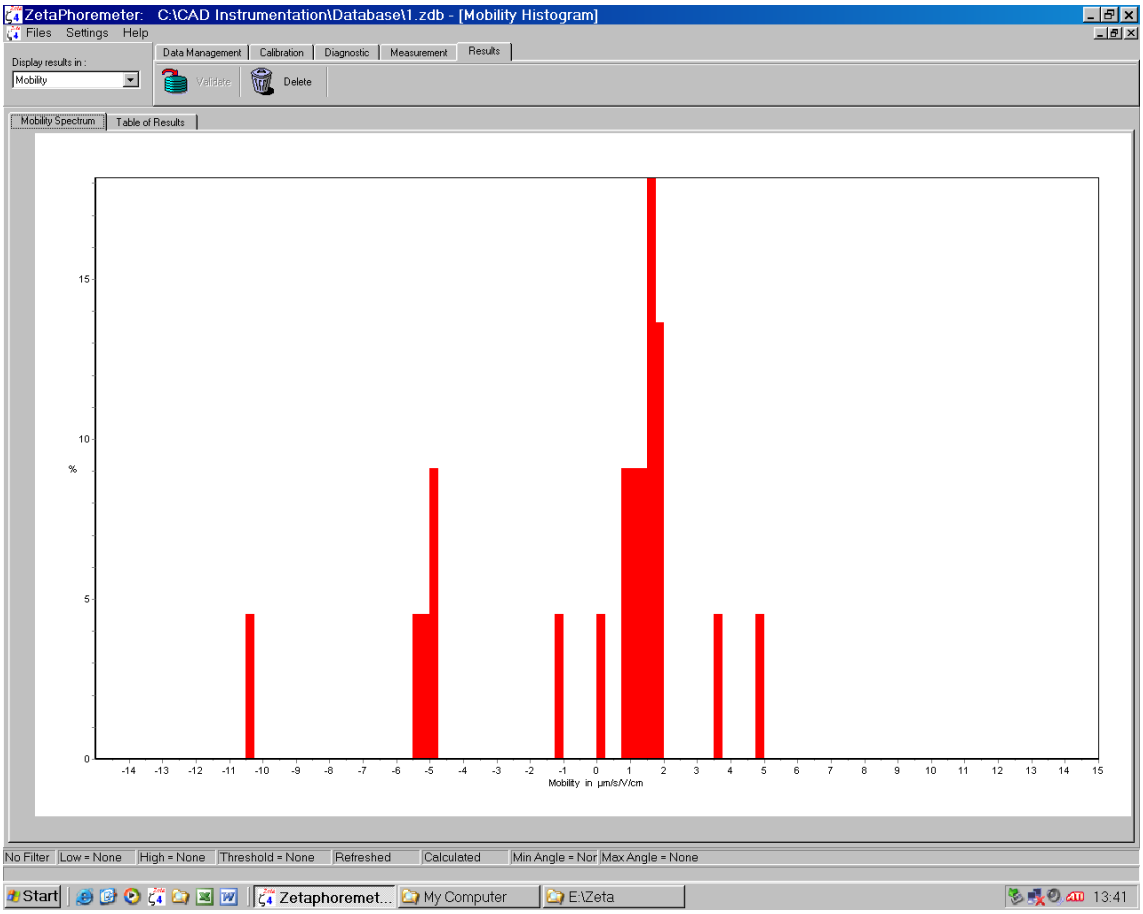


Figure 4. Electrophoretic mobility spectrum for 1 ml CNC_{BE} on quartz <5 µm at pH 8

2.6 Micro-flotation

The flotation of the mineral samples was done in a 100 ml Hallimond-tube flotation cell (Fig. 5) using 1 g of pure mineral in the size fraction 38-150 µm at the desired pH. The pH was adjusted using NaOH and HCl. The suspension of mineral in deionized water and the nano-entity was conditioned for 10 minutes, transferred to the Hallimond cell and floated for 1 minute at ambient temperature. If sodium oleate was added to the suspension, this was done after the initial conditioning time and 10 minutes of conditioning was added. For the experiments with MIBC, the frother was added in the last minute of the conditioning time. Both the floated particles and the un-floated particles were recovered by filtration. The flotation recovery was calculated as the mass-ratio between the recovered floated particles and the total amount of mineral particles.

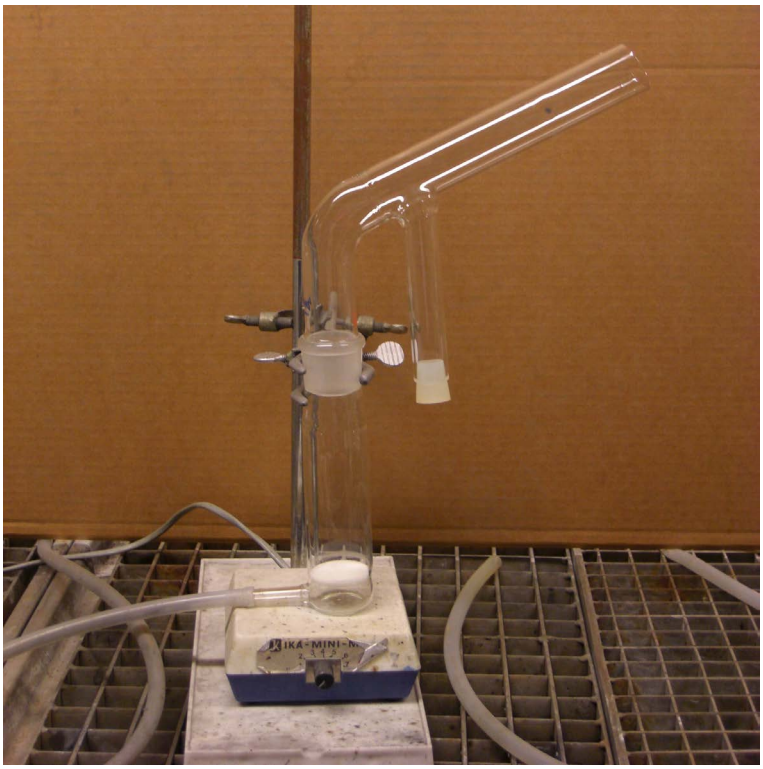


Figure 5. Hallimond Tube micro-flotation cell, 100 ml

2.7 Mini-flotation

The scale-up of the flotation was done in a 200 ml Claustahl cell (Fig. 6); using 80 g of either pure mineral or in a 40/40 mix of the pure minerals in the size fraction 38-150 μm at the desired pH. The pH was monitored during the entire conditioning and flotation time. Any pH adjustments were done using NaOH and HCl. The conditioning time was the same as in the micro-flotation where the mineral-nano mixture was conditioned for 10 minutes. When adding sodium oleate, 10 minutes was added to the conditioning time. If there was any addition of MIBC, then this was done in the last minute of the conditioning time. The flotation was facilitated by lightly helping the foam over the edge with a plastic spatula due to the cell only having an overflow in one direction and foam aggregating in the back of the cell. The concentrate and the tailings were decanted, filtered, and dried in an oven over night at 85 °C. The dry cakes were homogenized, weighed, and the densities of both products were measured separately in a He-pycnometer (micromeritics Accupyc II 1340). By knowing the densities of the products and the clean minerals, it is possible to calculate the grades of the products to establish a products balance.



Figure 6. Claustahl mechanical mini-flotation cell, 200 ml

3 RESULTS AND DISCUSSION

3.1 Characterisation of nano-entities

AFM images of CNC_{BE} (Figure 7, left) shows typical cellulose nano-crystal structure and the diameters were found to be in the range of 5-10 nm but are longer compared to typical wood based CNCs. The chitin nano-crystals (ChNC) had a diameter of 20 nm ± 10 nm and length of 300 nm ± 100 nm (Fig. 7, right).

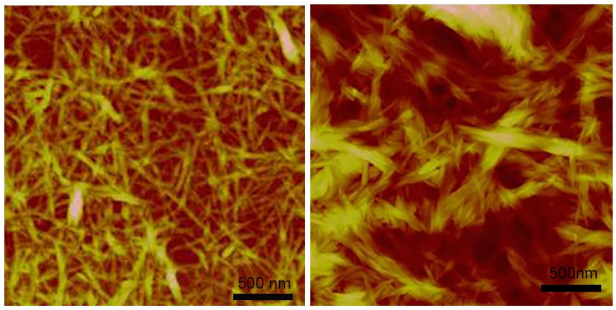


Figure 7. AFM images of used nano-entities; cellulose nano-crystals (left) and chitin nano-crystals (right)

Cellulose nano-crystals showed negative zeta potential in the whole range of pH, cf. Figure 8. ChNC on the other hand showed positive surface charge at acidic pH and negative surface charge at alkaline pH. Earlier studies have shown that the negative charge on CNC_{BE} can be attributed to carboxyl groups (Liu, et al., 2014). The positive surface charge on ChNC is due to amino groups whereas acetyl and carboxyl groups provide negative surface charge at alkaline pH.

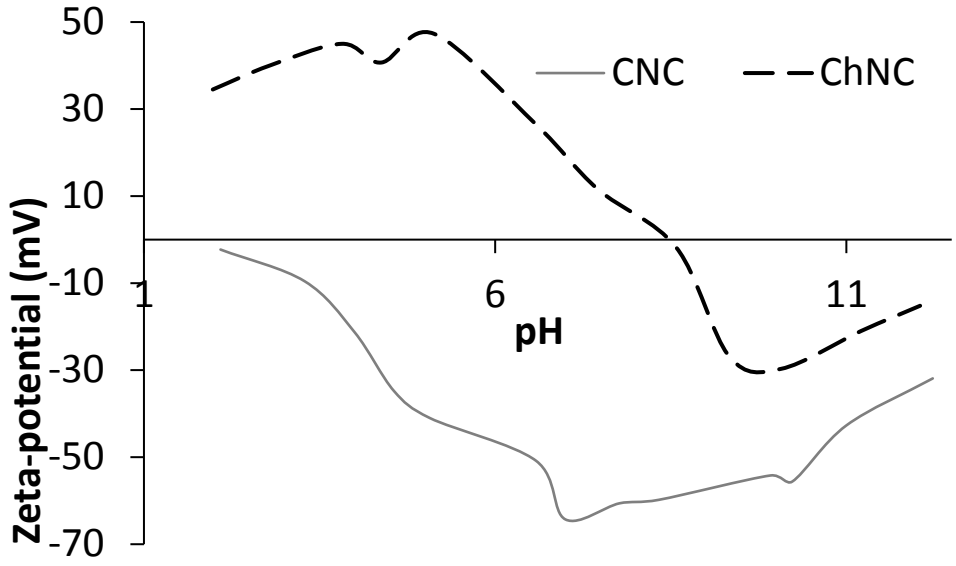


Figure 8. Zeta-potentials of pure nano-entities as produced

The isolation process is known to affect the surface charge content and the nature of the charge. Table 1 summarises the surface charge of the two materials used in this project (Liu, et al., 2015) and (Sehaqui, et al., 2014).

Table 1. Effect of isolation route on the surface characteristics of nanoparticles

Material	Source of nanoparticle	Preparation method	Surface charges (µmol/g)	Surface groups (qualitative analysis by ATR-FTIR)
CNC_{BE}	Bioethanol cellulose	Homogenization	151[#]	$-COO^-$
ChNC	Crab-shell powder	Hydrochloric acid hydrolysis	320*	- NH: $-COO^-$

[#]/ based on FTIR, */ based on titration

3.2 Baseline Zeta-potentials for minerals

The results from measurements on magnetite and quartz, <5 µm fractions, with just the background electrolyte $1 \cdot 10^{-3}$ M NaCl, are presented in Fig. 9. In this figure, and the following, all lines are B-splines that give a fair representation of the general trends in the data. The PZC for quartz is approx. 1.5 and for magnetite 5.5. These values are slightly lower than measured by other investigators.

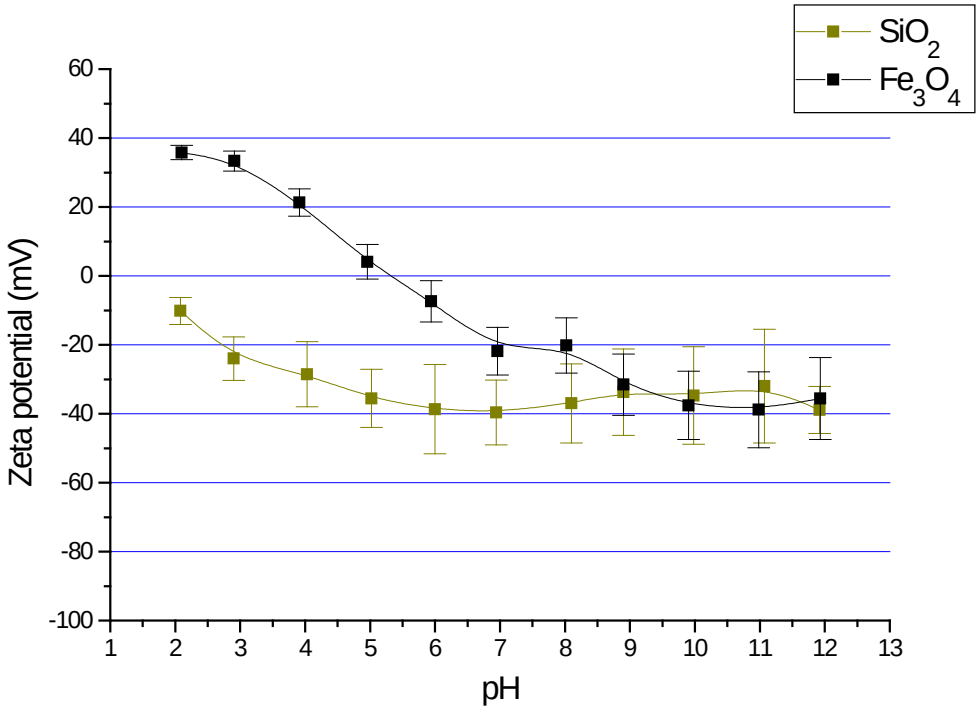


Figure 9. Zeta potential for quartz and magnetite as a function of pH, $1 \cdot 10^{-3}$ M NaCl

3.3 Nano-entities on quartz

From LTU/Material Science two samples of nano-entities were received with the following markings:

- Chitin crystals (ChNC), 1.7 %, said to have a surplus of amine groups,
- CNC_{BE}, 2 %, having more of carboxylic groups.

Both samples were liquids; ChNC was low-viscous having the look of fine meal in water, while the CNC_{BE} was clear and high-viscous. This also made the CNC_{BE} hard to dispense, since it stuck to the outside of the pipettes.

The measurements on quartz are presented in Fig. 10. ChNC gives strong charge reversal for quartz for the two strongest concentrations (1 and 0.1 ml) investigated. CNC_{BE} does not significantly alter the quartz surface.

The actual molar concentration of active groups in the nano-cellulose is not well known. Previous experiments with designed collector molecules (Karlkvist et al., 2015) were done in the concentration range 10^{-5} M to 10^{-3} M. It is a qualified guess that 1 ml of the ChNC solution will correspond to about 10^{-4} M. It was found out; however, that ChNC at this level also gave a charge change on magnetite. Therefore, a second series of measurements were made with addition of 0.1 ml only. The charge reversal for quartz with ChNC is nearly the same at both addition levels. The only difference is that the standard deviation is slightly smaller for the lower addition, indicating maybe less of an over-dosage, and thereby less free nano-entities.

A third series with only 0.01 ml ChNC showed that the zeta-potentials became closer to the ones for the pure quartz, thus indicating an addition level not occupying all surface sites.

CNC_{BE} did not markedly change the Zeta potential of quartz. No attempt to lower the addition of CNC_{BE} on quartz was made, since this nano-cellulose solution is viscous and hard to dispense in low volumes.

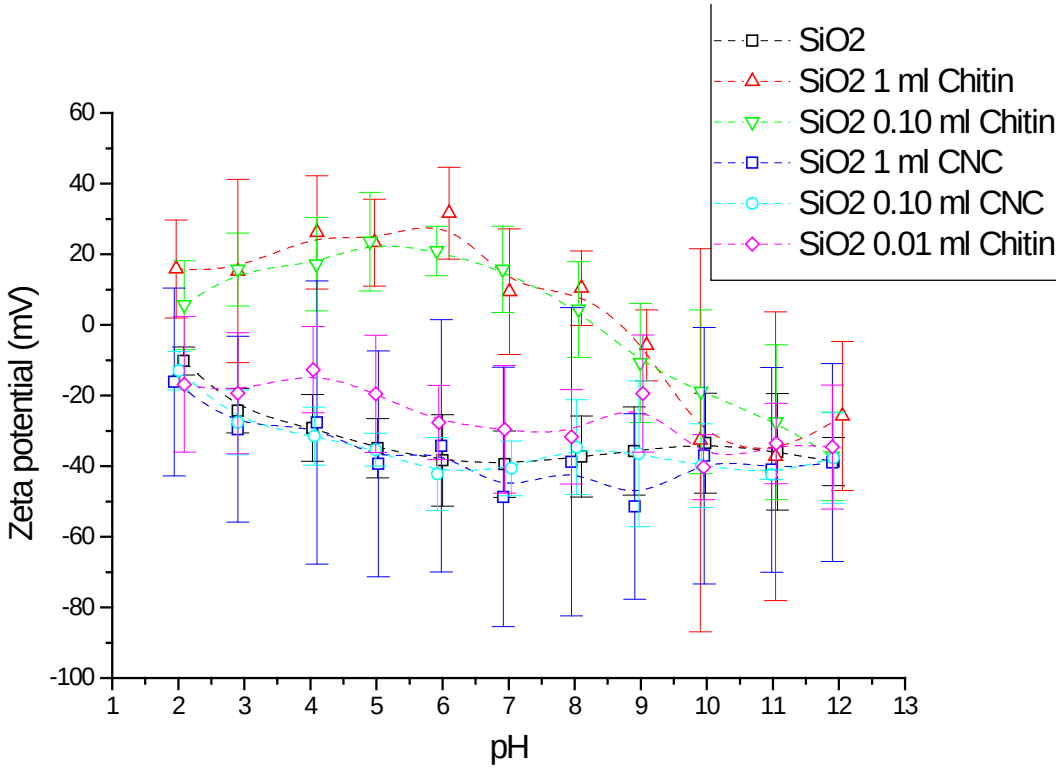


Figure 10. Zeta potential for quartz with nano-entities as a function of pH, $1 \cdot 10^{-3}$ M NaCl

3.4 Nano-entities on magnetite

The measurements on magnetite are presented in Fig. 11. Both ChNC and CNC_{BE} give charge changes for magnetite. The magnitude of the changes are somewhat smaller than for quartz. However, the curves for ChNC on quartz and magnetite are close, and the same applies for CNC_{BE} on the two minerals, cf. Fig. 12 and Fig. 13.

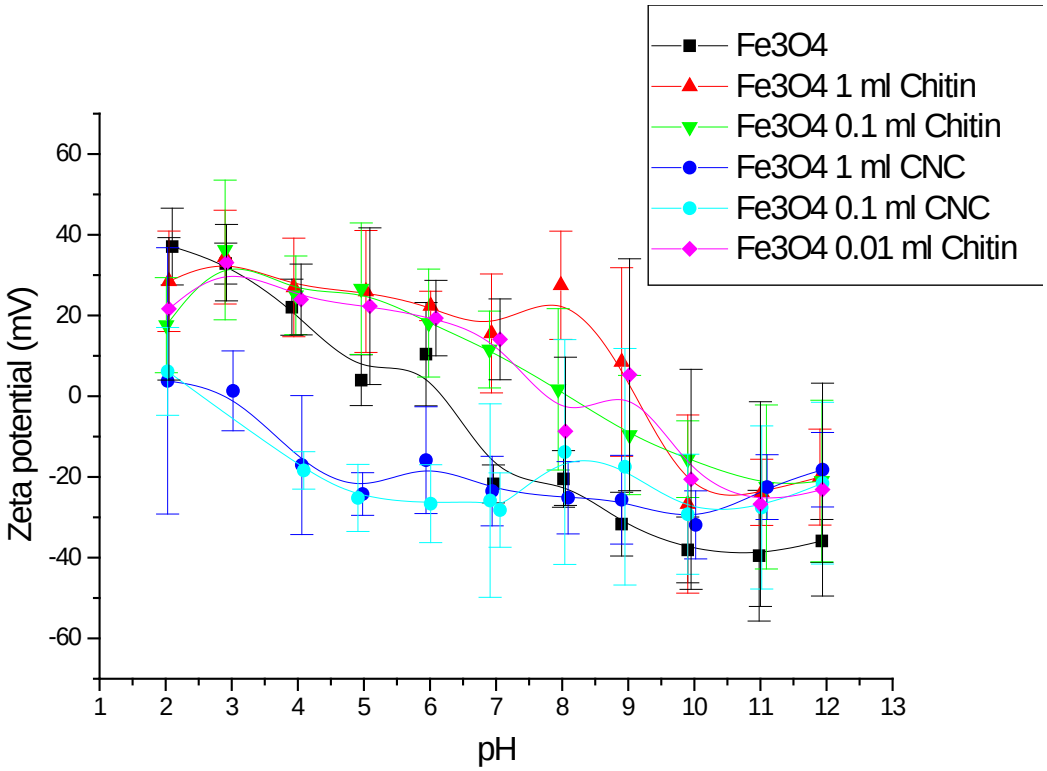


Figure 11. Zeta potential for magnetite with nano-entities as a function of pH, $1 \cdot 10^{-3}$ M NaCl

3.5 ChNC

The measurements with ChNC on quartz and magnetite are presented together in Fig. 12. Error bars are removed for clarity. The curves for 1 and 0.1 ml additions are overlapping for most pH values, only for pH 8 there is some difference, but it is probably too small to be practically usable. However, there is a larger difference for 0.01 ml ChNC.

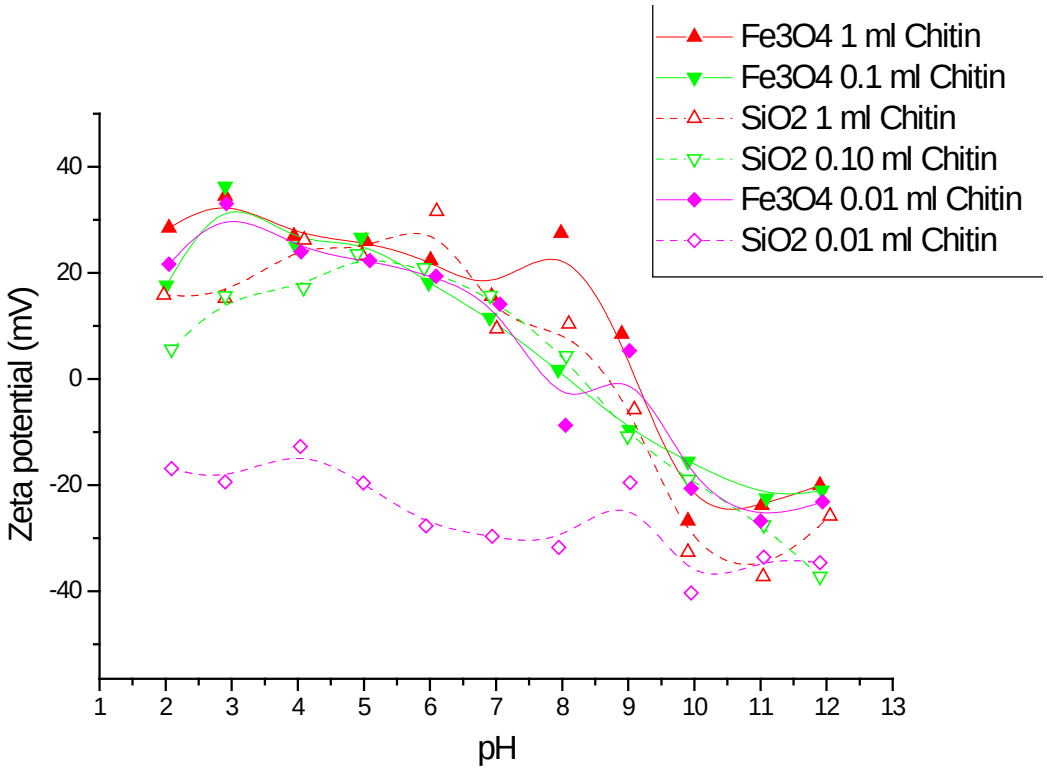


Figure 12. Zeta potential for ChNC on quartz and magnetite as a function of pH, $1 \cdot 10^{-3}$ M NaCl

3.6 CNC_{BE}

Measurements with CNC_{BE} on both quartz and magnetite are presented in Fig. 13. Error bars are removed for clarity. It is interesting to note that quartz with CNC_{BE} is consistently about 20 mV lower than the corresponding magnetite curve. But both curves are on the negative side in the pH range of interest. This implies that it would not be easy to achieve selective anionic activation of quartz with CNC_{BE}.

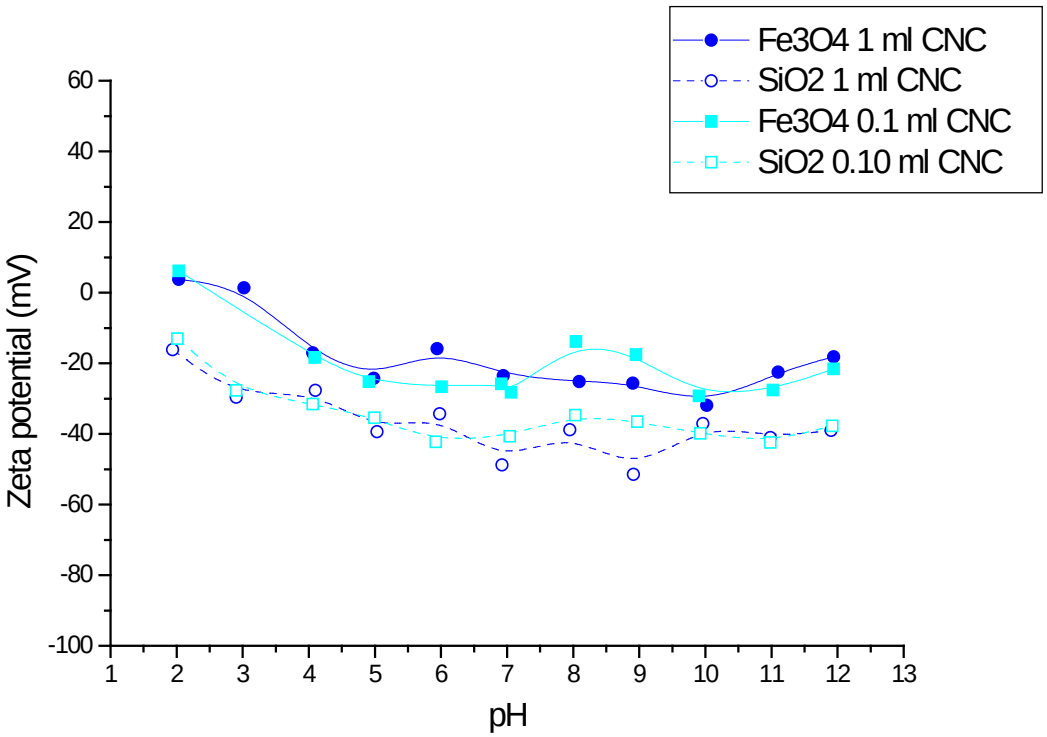


Figure 13. Zeta potential for CNC_{BE} on quartz and magnetite as a function of pH, $1 \cdot 10^{-3}$ M NaCl

3.7 Micro-flotation studies

3.7.1 Nano-entities alone

The micro-flotation studies were all made in the 100 ml Hallimond tube. The idea was to check if there might be any systematic difference between nano-entities and minerals in flotation over the pH range of interest. Figure 14 shows that there are hardly any difference between the nano-entities. In tests on magnetite, it was not possible to use stirring by a small magnet, therefore, the results for magnetite are consistently lower than for quartz.

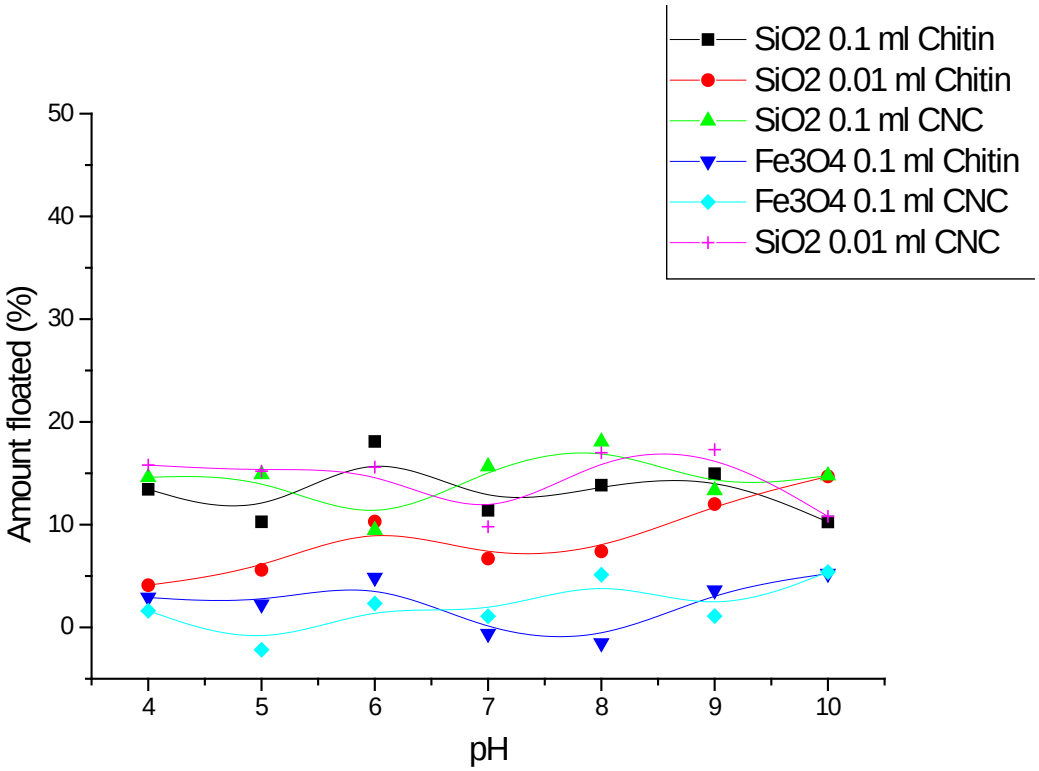


Figure 14. Micro-flotation results as function of pH

3.7.2 Nano-entities with flotation reagents

Since it is not clear if the nano-entities in themselves are hydrophobic or hydrophilic or whether they will change the hydrophobic/hydrophilic balance on the surface, a few experiments with collector and/or frother were done. The idea was to check if the nano-entities might be just the contact point on the mineral surface, i.e. a surface complexing agent/cationic activator, to which the collector could attach.

The tests were all made for addition rate 0.1 ml of the nano-entities. In tests with frother alone, 0.05 ml of MIBC were added. If both frother and collector were added, the MIBC addition stayed the same, but 0.2 ml of a 2.5 wt-% Na-oleate solution was added.

The results with nano-entities on quartz are presented in Figure 15 (ChNC) and Figure 16 (CNC). There are hardly any difference between using the nano-entity and adding a frother. It means that the nano-entity itself has little influence on the hydrophobic/hydrophilic balance on the quartz mineral surface. With the addition of oleate, the flotation increases. This point to the possibility that the nano-entities might act as surface complexing agents on the quartz mineral surface, leading to cationic activation of the surface. From Fig. 15 there is also an indication that ChNC at pH 8 could give slightly higher quartz micro-flotation.

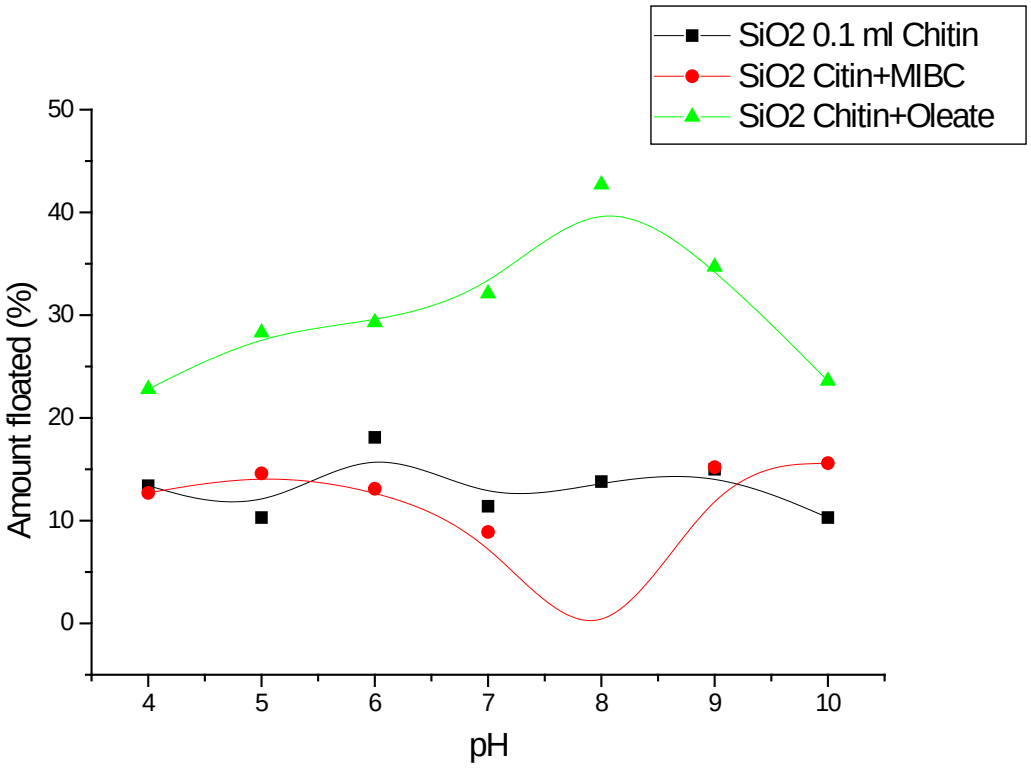


Figure 15. Micro-flotation of quartz with ChNC

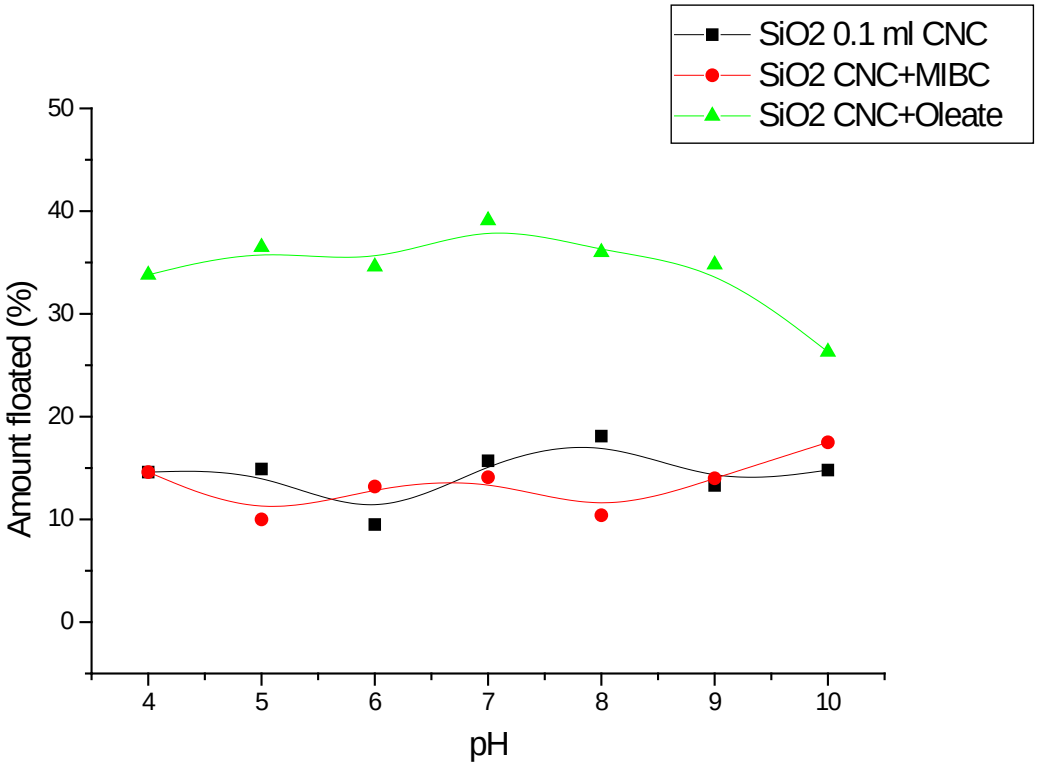


Figure 16. Micro-flotation of quartz with CNC_{BE}

The same experimental conditions were applied for micro-flotation of magnetite. The results are presented in Figure 17 (ChNC) and Figure 18 (CNC_{BE}). For ChNC + oleate the flotation was slightly higher, but not to the same extent as for quartz.

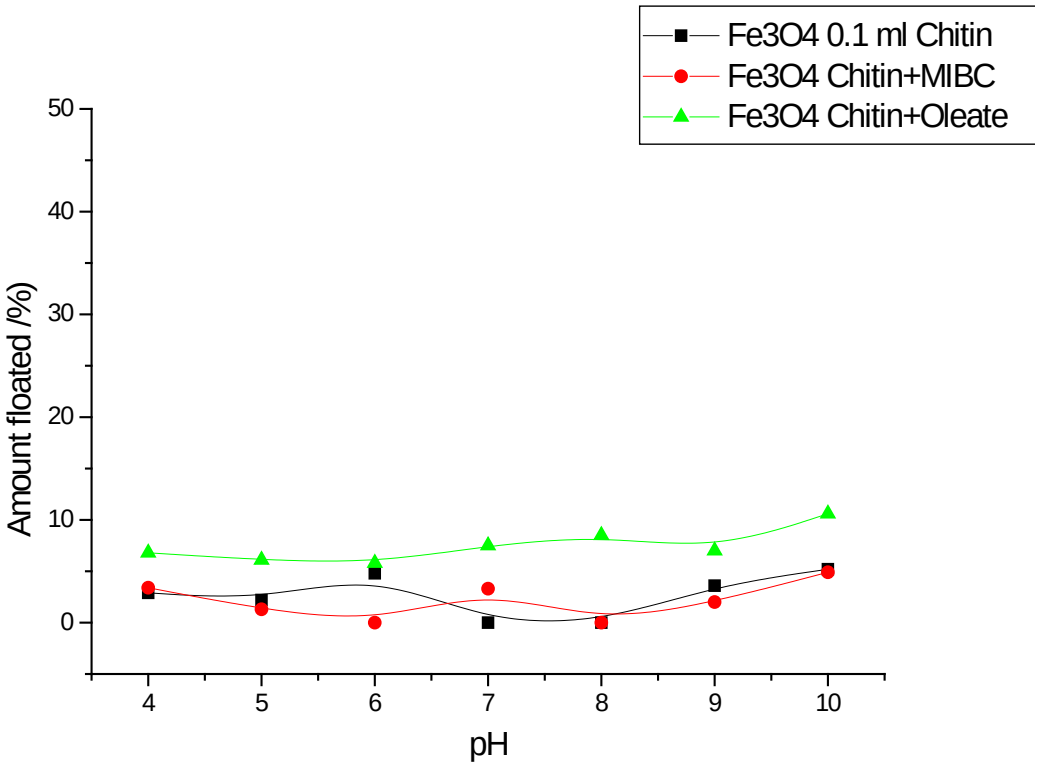


Figure 17. Micro-flotation of magnetite with ChNC

Since ChNC at the lowest addition level (0.01 ml) did show a much-changed Zeta-potential curve for quartz, a few micro-flotation tests were done for this condition, cf. Fig. 18. There is no difference between micro-flotations for ChNC with and without frother.

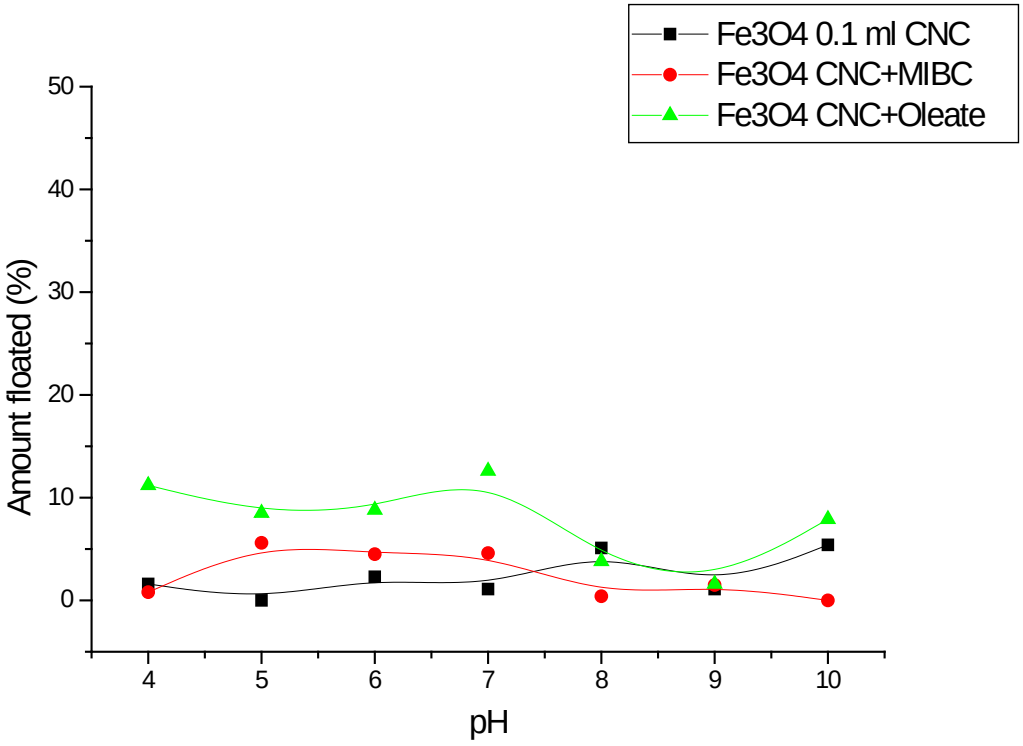


Figure 18. Micro-flotation of magnetite with CNC_{BE}

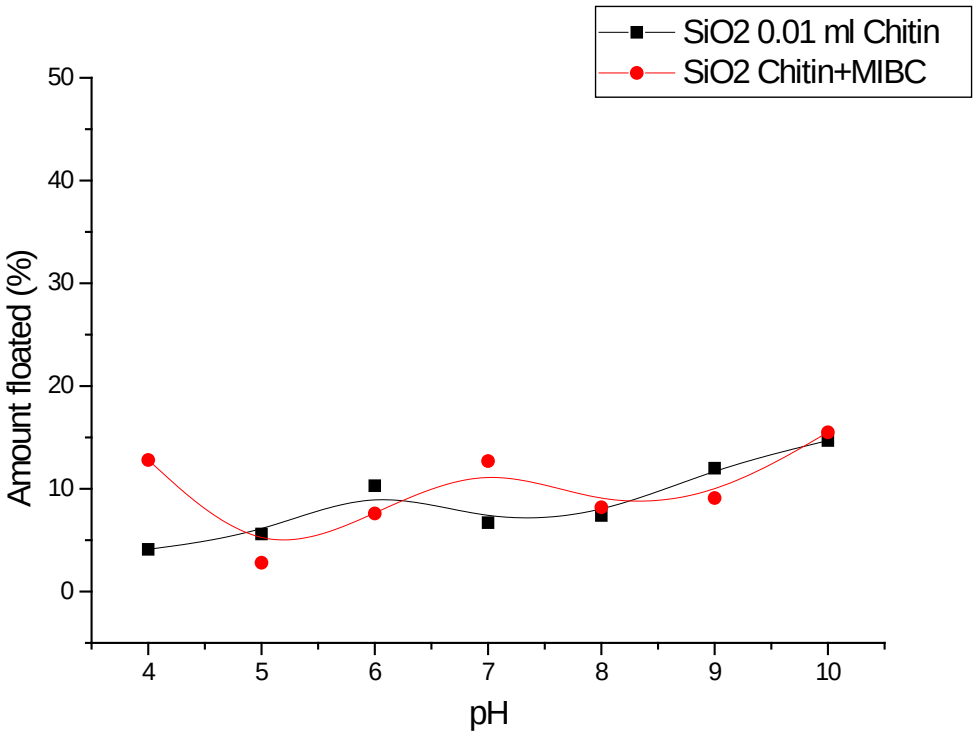


Figure 19. Micro-flotation of quartz with lowest addition of ChNC

3.7.3 Nano-entities and particle mixtures

The single mineral micro-flotations did show that a combination of nano-entity (ChNC), collector and frother gave the highest recoveries. Therefore, a series of tests were run with 1 g quartz + 1 g magnetite in the Hallimond cell, cf. Figure 20. The tests were run at pH 8, since this pH has shown some differences in Zeta-potential and micro-flotation for the single minerals. The idea was to check if combining the minerals, they could influence each other in the micro-flotation. As expected, flotation with only ChNC gave the lowest amount floated, ChNC + oleate an intermediate result, and all reagents combined gave the highest. Comparing the results with the ones for the single minerals reveals the single mineral micro-flotations gave a slightly higher amount floated. The reason for this is probably that the reagent additions were kept constant, and in the single mineral cases it meant that, the surface concentrations became higher, leading to more materials floating.

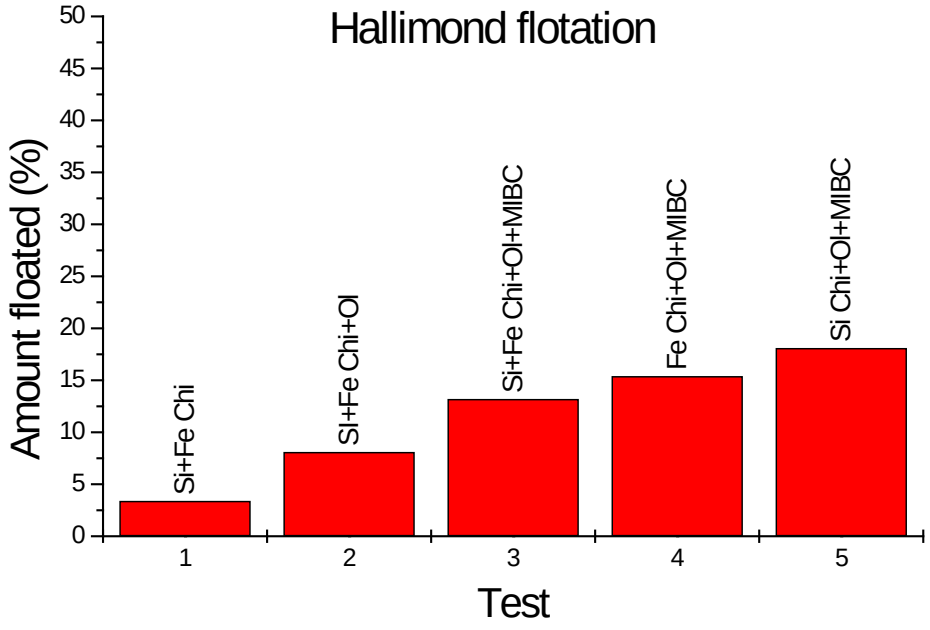


Figure 20. Micro-flotation tests with binary mixtures of magnetite and quartz

3.8 Mini-flotation studies

The results from zeta-potential measurements and micro-flotation studies were not entirely conclusive, but indicated that there might be some difference around pH 8. Therefore, four flotation tests were made in a very small mechanical flotation cell, a 200 ml Claustahl cell. The reason for doing this was that this cell offers hydrodynamic conditions closer to full-scale flotation, and that the ratio between reagents and solids are more realistic.

All flotation test were run with 40+40 g of quartz and magnetite giving a dilution around 33 wt-% solids, and at pH 8. The additions recalculated to g/ton were:

- ChNC 850 g/ton
- Oleate 200 g/ton
- MIBC 1 g/ton

Four tests with mineral mixtures could be completed with the material available:

- Test with only ChNC addition
- Test with ChNC + MIBC
- Test with ChNC + oleate
- Test with ChNC + oleate + MIBC

Since the flotation feed was a binary mixture of magnetite and quartz, it became possible to analyse the grade of the minerals in the flotation products by checking the densities of the products, and then back-calculating to mineral grades. An example for flotation with only ChNC is in Fig. 21.

Luleå University of Technology — Products Balance — Account

Div. of Mineral Processing — Test No.

Date

Material: Magnetite + Quartz 50/50 — Treatment: — Signature

Product		Weight			Assays		Contents (g)		Distributions (%)	
Notation	Name	(g)	(%)	ρ	Magn	SiO_2	Magn	SiO_2	Magn	SiO_2
1	Conc	6.9	8.6	2.6908	4.72	95.28	0.326	6.574	0.8	16.8
mp 4	Tailings	73.1	91.4	3.6003	55.36	44.64	40.469	32.631	99.2	83.2
Calc.Feed		80.0	100.0		50.99	49.01	40.795	39.205	100.0	100.0

	$\rho_{magnetite}$	5.1282	16.0
	ρ_{quartz}	2.6289	

$$\%Magn = \frac{\left(\rho_m - \frac{\rho_m \cdot \rho_q}{\rho_{sample}}\right)}{\left(\rho_m - \rho_q\right)} \cdot 100$$

Figure 21. Products balance from density measurements

The flotation tests are evaluated with five parameters in Figure 19:

- The percentage of SiO_2 in the concentrate, how clean the concentrate is;
- The recovery of SiO_2 to concentrate;
- The Difference Index (DI), the difference in the distributions of quartz and magnetite to concentrate;
- The percentage of magnetite in the concentrate;
- The recovery of magnetite to the concentrate.

The results in Figure 22 reveals that the highest grade of quartz in the concentrate was achieved with ChNC only. It became slightly lower if a frother was added. When oleate was added to the flotation the selectivity was lost, and both minerals floated. One possible explanation for this can be an over-dosage of oleate. Although, the addition rate (200 g/t) is reasonable for an oxide mineral system, the particles were 38-150 µm implying a low specific surface area, and by that a possible over-dosage of collector. This might have led to oleate-induced flotation of magnetite by chemisorption to Fe(II) sites in the magnetite surface.

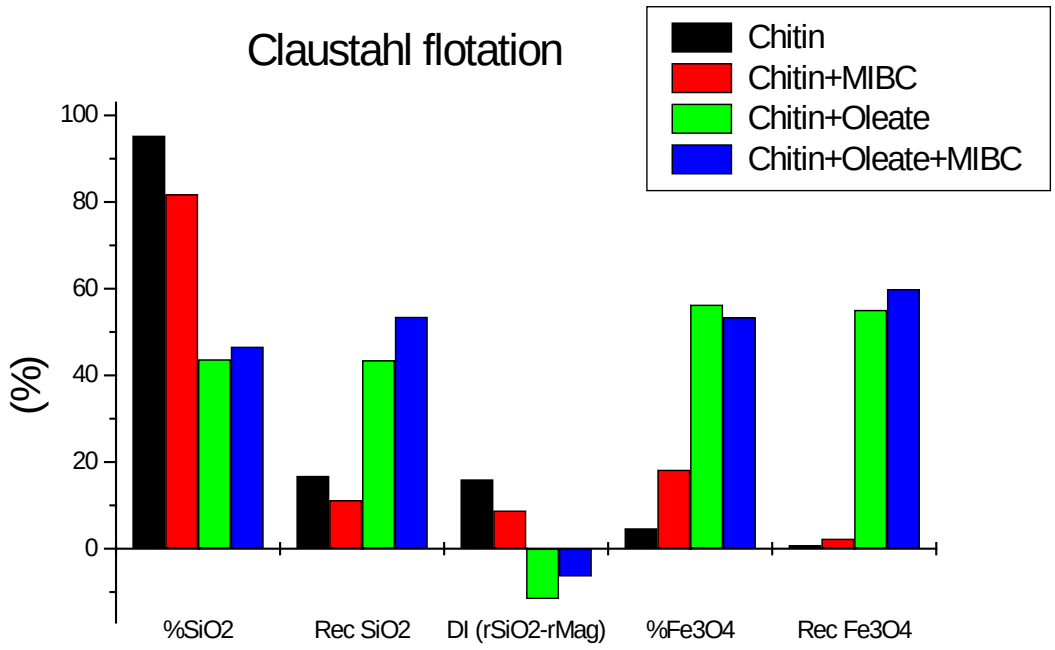


Figure 22. Results from mini-flotation tests at pH 8

4 CONCLUSIONS

The results are interesting in the way that they clearly show that both nano-entities strongly adsorb on the surface causing charge reversals. However, the adsorption appears to be largely non-preferential for the investigated minerals over the pH and concentration ranges investigated.

For the CNC_{BE} the result is slightly more interesting, since the Zeta potential for quartz is more or less constantly 20 mV lower than for magnetite over the pH range investigated. It might open up for using CNC_{BE} for anionic activation of quartz, but this would imply the use of a cationic flotation collector, and this is probably not desirable.

Micro-flotation results show that both the nano-entities float quartz to the same extent, and that the same is true for magnetite. However, the amount floated is higher for quartz. There is also an indication that ChNC at pH 8 can have some preference for quartz over magnetite. The same seems not to be the case for CNC_{BE}.

Mini-flotation results at pH 8 for mineral mixtures with ChNC and flotation reagents show that ChNC can selectively float quartz for the given conditions, but the recovery is low. If oleate is added, the selectivity is lost. This means that the nano-entity is probably not a cationic activator, rather it induces some little hydrophobicity to the quartz surface on its own.

Oleate might have been added in excess, leading to the unwanted magnetite flotation.

5 RECOMMENDATIONS FOR FURTHER WORK

A better understanding of the number of functional groups per molecular mass of the nano-entities is needed to be able to have a better estimate of the concentration of active sites in the nano suspension. In addition, nano-entities with preferably only one functional group must be produced and tested. In this context, Tempo modified nano-cellulose and cationic nano-cellulose can be used in future experiments.

Mini-flotation seems to be the best way to test for selectivity in the quartz-magnetite system. However, it cannot be done with binary mixtures of pure minerals since the consumption of these are more than available. Instead, magnetite ores with high natural quartz content must be used. It also means that it will be possible to have realistic grinding conditions to produce flotation feeds with practical relevance.

Flotation tests on mini-scale with different nano-entities must be done to check whether the selective flotation with ChNC is due to its dominating polar group(s), or if it adsorbs to the mineral surface by non-polar attraction. The addition levels must be checked.

The interaction with frother and collector must be checked over a wide range of pH, and addition rates.

Since the main idea of using nano-entities is that they may replace amines in silicate flotation, their toxicity to aquatic life must be investigated.

6 ACKNOWLEDGEMENT

The project was funded by Vinnova grant 2015-01300, and was part of Vinnova's Strategic Innovation Programme "Mining and metal winning".

Dr. Lee Goetz is acknowledged for producing the nano-entities.

7 REFERENCES

Karlkvist, T., Patraa, A., Rao, K.H., Bordes, R. and Holmberg, K., 2015. Flotation selectivity of novel alkyl dicarboxylate reagents for apatite–calcite separation, *Journal of Colloid and Interface Science* 445:40-47. http://dx.doi.org/10.1016/j.jcis.2014.11.072

Mathew, A.P., Oksman, K., Karim, Z., Liu, P., Khan, S.A., and Naseri, N., 2014. Process scale up and characterization of wood cellulose nanocrystals hydrolysed using bioethanol pilot plant. *Ind. Crop. Prod.* 58:212-219.

Nair, K.G. and Dufresne A., 2003. Crab shell chitin whisker reinforced natural rubber nanocomposites. 1. Processing and swelling behavior. *Biomacromolecules*, 4:657-665.

Laitinen, O., Kemppainen, K., Ämmälä, A., Sirviö, J.A., Liimatainen, H., and Niinimäki, J., 2014. Use of Chemically Modified Nanocelluloses in Flotation of Hematite and Quartz. *Ind. Eng. Chem. Res.* 53:20092-20098.

Laitinen, O., Hartmann, R., Sirviö, J.A., Liimatainen, H., Rudolph, M., Ämmälä, A. and Illikainen, M., 2016. Alkyl aminated nanocelluloses in selective flotation of aluminium oxide and quartz. *Chem. Eng. Sci.* 144:260-266.

Liu, P., Sehaqui, H., Tingaut, P., Wichser, A., Oksman, K. and Mathew, A.P., 2014. Cellulose and chitin nanomaterials for capturing silver ions (Ag^+) from water via surface adsorption. *Cellulose* 21:449-461.

Liu, P., Borrell, P.F., Božič, M., Kokol, V., Oksman, K, and Mathew, A.P., 2015. Nanocelluloses and their phosphorylated derivatives for selective adsorption of Ag^{+}, Cu^{2+} and Fe^{3+} from industrial effluents, *J. Hazard Mater*. 294:177-185.

Sehaqui, H., de Larraya, U.P., Liu, P., Pfenninger, N., Mathew, A.P., Zimmermann, T. and Tingaut, P., 2014. Enhancing adsorption of heavy metal ions onto biobased nanofibers from waste pulp residues for application in wastewater treatment, *Cellulose* 21:2831-2844.

Sirviö, J.A., Visanko, M., Laitinen, O., Ämmälä, A. and Liimatainena, H., 2016. Amino-modified cellulose nanocrystals with adjustable hydrophobicity from combined regioselective oxidation and reductive amination. *Carbohydrate Polymers* 136:581–587.