

Supporting Information

Agglomeration of Cellulose Nanocrystals: The Effect of Secondary Sulfates and Their Use in Product Separation

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Karl Fischer titration

The water content of cellulose was determined by volumetric Karl Fischer titration (TitroLine KF, Xylem Analytics, Weilheim, Germany). All chemicals were purchased from Carl Roth (Karlsruhe, Germany). The iodine titrant (Roti®hydroquant C5; 5 mg H₂O mL⁻¹, free of pyridine) was determined with the water standard (Roti®hydroquant; 10 mg H₂O g⁻¹). Methanol (Roti®hydroquant D; dry) and formamide (99.5%) were used as solvent in a volume ratio of 1.5 : 1. About 0.3 g of cellulose was added to the solvent. The titration was started when the sample was completely dissolved. The solvent was exchanged after each measurement.

Concentration determination by UV-Vis spectrophotometry – validity of approach

UV-Vis spectra of H-CNCs of different concentrations

A stock solution of 1 wt.% H-CNCs was prepared and UV-Vis absorbance spectra between 0 and 1 wt.% were recorded in the λ range of 200 to 500 nm (see **Fig. S1a**). Linearity of $A(\lambda, c)$ vs. c was best between 229 and 476 nm ($R^2 \geq 0.99$). Thus, data evaluation was done in the λ range between 250 and 450 nm. The mean absolute error of the library was 0.9% and 0.5% for CNC concentrations > 0.1 wt.%. The mean wavelength exponent n of all spectra was 3.354 ± 0.012 and the mean scattering coefficient k was 0.151 ± 0.008 .

For H-CNCs, a slight decrease of k was observed from $k_{c \rightarrow 0} = 0.167 \pm 0.010$ with a rate of $-0.044 \pm 0.003 \text{ g}_{\text{CNC}}^{-1}$. The concentration-dependent change of k might be induced by the increasing probability of multiple scattering with increasing particle concentration. However, the error introduced to the evaluation was negligible.

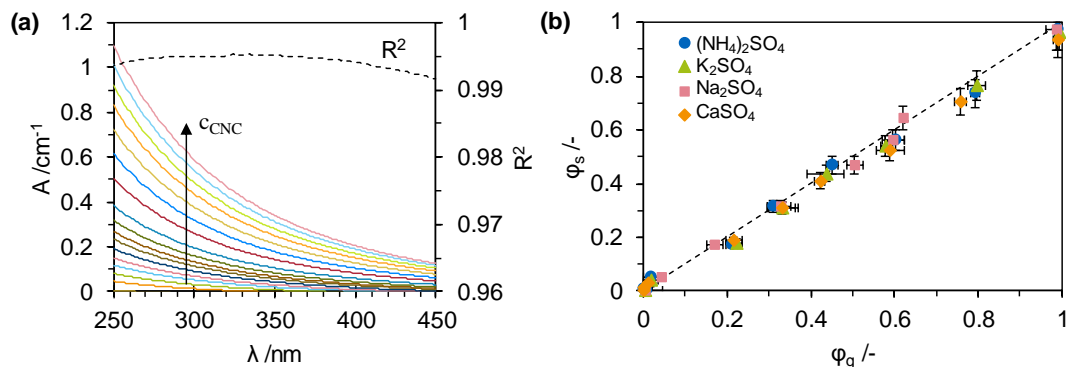


Fig. S1 Absorbance spectra of H-CNCs between 0 and 1 wt.% (a) and correlation of spectroscopically and gravimetrically determined CNC concentration (b)

UV-Vis spectra of CNCs in the presence of salts

In the presence of salt, the wavelength coefficient increased slightly for all investigated salts (see **Fig. S2**). Towards high ionic strengths, n increased strongly, which might indicate cluster growth.

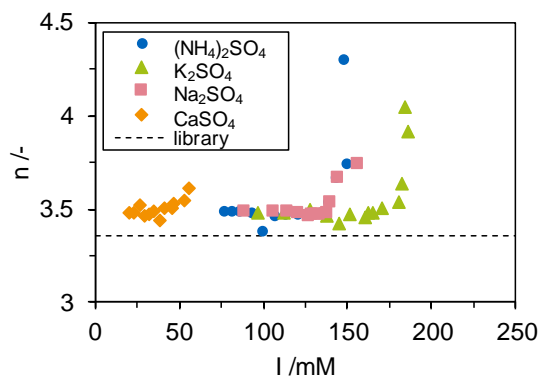


Fig. S2 Wavelength coefficients of CNCs in the presence of different salts and varying salt concentrations

The validity of the determination of CNC concentration was checked by correlating the mass fraction of CNCs derived from the spectra library φ_s and the gravimetrically determined mass fraction of the respective aliquot φ_g (see **Fig. S1b**). The data was in good agreement and therefore the spectra library is seen as suitable to determine the concentration of colloiddally stable CNCs in the presence of salts.

Particle size distributions with a_{eq} , recalculated from L_{mean} and a reasonable range of values for W (5 - 20 nm) as well as the mean hydrodynamic apparent particle diameter, were set up to model the respective absorbance spectra. No interparticle interaction and equal probability of all orientational scattering states of the particles was assumed. Resulting wavelength exponents of $n \approx 4$ indicated

an underestimation of the actual scattering area or the polydispersity of the CNCs. Thus, information from ex-situ TEM or DLS are not suitable to model the actual absorbance profile of scattering of CNCs. One-dimensional absorbance data furthermore cannot be used for the conclusion of geometrical information of CNCs without additional boundary conditions that cannot be reasonably assumed and therefore other methods must be used, for example small-angle neutron scattering (Mohraz et al. 2004, Cherhal et al. 2015).

UV-Vis absorbance spectra are suitable to comparably detect changes of the size distribution of a particulate system, but not to deduce the origin, type, or extent of change. It must be taken into consideration that a change of n – for example by particle growth or agglomeration – also affects turbidity-based determinations of concentration, albeit deviations may be minor.

Water consumption

Dialysis

The conductivity of the wastewater during dialysis of H-CNCs decayed exponentially to $30 \mu\text{S cm}^{-1}$ after 166 h and the exchange of 83 L of water (see **Fig. S3**).

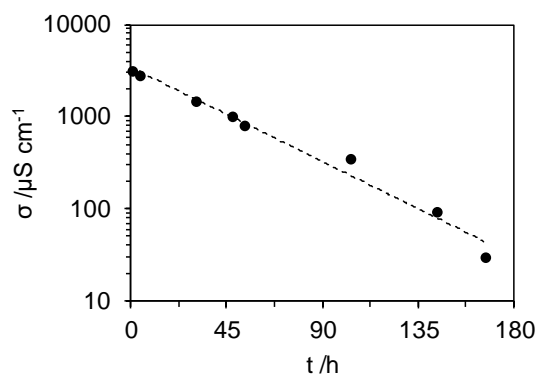


Fig. S3 Water consumption during dialysis of H-CNCs

Comparison of water consumption during downstream processing

The non-optimized production processes of H-CNCs, NH_4 -CNCs, K-CNCs, Na-CNCs and Ca-CNCs were evaluated (see **Fig. S4**). It must be noted that while the water consumption of quenching and centrifugation for H-CNCs is more or less fixed, the water consumption of the neutralized products can vary strongly depending on the point of neutralization (for example after hydrolysis or after first

centrifugation) and the choice of counterion, resulting in secondary sulfates of varying solubility. However, the water consumption for any purification strategy is strongly dependent on the cellulose-to-CNC conversion ratio and will be in the range of several hundred to thousand g of H₂O per produced g of CNCs.

Extensive dialysis brings the water consumption up to several tens of kg of H₂O per produced g of CNC. Thus, improving water consumption or recycling waste water from dialysis is worth considering.

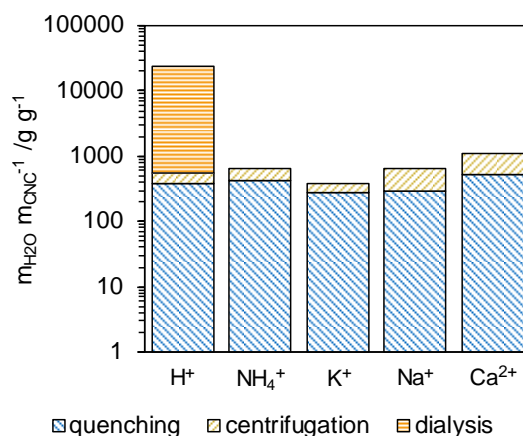


Fig. S4 Water consumption of unit operations per gram of CNC produced

References

- Cherhal F, Cousin F, Capron I (2015) Influence of charge density and ionic strength on the aggregation process of cellulose nanocrystals in aqueous suspension, as revealed by small-angle neutron scattering. *Langmuir* 31(20):5596–5602
- Mohraz A, Moler DB, Ziff RM, Solomon MJ (2004) Effect of monomer geometry on the fractal structure of colloidal rod aggregates. *Physical review letters* 92(15):155503