Phosphorylation of nanocellulose and its application potencials

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✓ To compare
  ✓ enzymatic vs.
  ✓ chemical (hetero-/homo-geneously via hydrolys, via carboxyls)
phosphorylation (introd. anionic phosphate ester gr. -PO$_3^{2-}$) approaches of
✓ cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC)

✓ To characterize phosphorylation efficacy and stability

✓ To establish structure- morphology-properties relationship

✓ To utilize phosphorylated properties ⇒ potential applications
**Enzymatic vs. Chemical (on Cell-OH / COOH groups)**

Hexokinase-mediated using ATP/Mg$^{2+}$ vs. By using H$_3$PO$_4$ in water or molten urea

13C –NMR spectroscopy
Phosphorylation occurred at C6-OH group of the glucose, resulting to minor crystal structure reduction.

13C –NMR spectroscopy
Phosphorylation occurred at C6, C2 and/or C3-OH groups of the glucose, resulting to huge crystal structure reduction.

ATR-FTIR spectroscopy
Two IR bands at 2360 cm$^{-1}$ (P-H) 1210 cm$^{-1}$ (P=O)

Potentiometric titration
Two inflexion points in the ratio of 1:2

**The same structure of functional groups confirmed by both process!**
**Quatification & stability of \(-\text{PO}_3^{2-}\) groups /**

<table>
<thead>
<tr>
<th></th>
<th>CNF</th>
<th></th>
<th>CNC</th>
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<tbody>
<tr>
<td></td>
<td>(-\text{PO}_3^{2-}) mmol/kg</td>
<td></td>
<td>(-\text{COO}^-) mmol/kg</td>
<td></td>
</tr>
<tr>
<td>REF</td>
<td>0</td>
<td>73±4</td>
<td>0</td>
<td>151±6</td>
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<tr>
<td>Enzymatic</td>
<td>154±11</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>Hex+ATP</td>
<td></td>
<td></td>
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<tr>
<td>Chemical on OH gr.</td>
<td>18±2</td>
<td>Confirmed by FTIR</td>
<td>435±7</td>
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<tr>
<td>(\text{H}_3\text{PO}_4/\text{water})</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(\text{H}_3\text{PO}_4/\text{molten urea})</td>
<td>1173±26</td>
<td></td>
<td>1038±9</td>
<td></td>
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<tr>
<td>Chemical via COOH gr.</td>
<td>1500-2500</td>
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- **Expensive & in-reusable Hex/ATP**
- **Difficulty washed-out ATP**
- **no effect on crystallinity**
- **Di- and tri-substituted esters with CNF can be formed, yielding to insoluble products.**
- **No changing in crystalline structure.**
- **HYDROLYSIS is pronounced at high-molar (\(>10\text{mM}\)) acidic (pH<3, HCl) or alkaline (pH>8, NaOH) mediums.**
- **Very stable linkage**
- **Reusable treating bath (monomers)**

P-CNFs/CNCs form well dispersed particles between pH 4.5-10.5.

\[ pK_1 (pH \approx 7.3) : \text{CNF-O-PO}_3\text{H}_2 \leftrightarrow \text{CNF-O-PO}_3\text{H}^- \]

\[ pK_2 (pH \approx 12.5) : \text{CNF-O-PO}_3\text{H}_2 \leftrightarrow \text{CNF-O-PO}_3^{2-} \]

P-CNFs/CNCs form well dispersed particles between pH 4.5-10.5.

pCNF shown an increased adsorption capacity towards more alkaline region (pH > 7)
Flame-retardant properties (biobased nano-composites)

![Graph showing weight loss and heat flow](Image)

- Native-CNF
- Phosph-CNFM (10.7M H3PO4)
- Phosph-CNFM (Molten urea+H3PO4)
- Phosph-CNFM HEX (250mM MgCl2)

Native CNF

Phosphorylated-CNF

![Scanning electron microscopy images](Image)
Biomineralization potential (hydroxyapatite growth)

- after 10 days of exposure to simulated body fluid (SBF) at 37°C

Native CNF

Phosphorylated CNF

GEL alignment induced by CNF self-assembling

Gelatin+CNF

Gelatin+p-CNF

- pCNF-orientation is disturb after mineralization
- Mineralization process is induced by pCNF presence and location
High and selective adsorption of heavy metals & cationic dyes ⇒ Ion-exchange filtration performance

Mix bio-nanomaterials with Fe²⁺ Cu industrial wastewater (pH=7)

Des. 99%
Des. 69%
Des. 75%

Adsorption kinetic [%]

0,1 1 10 100

0 20 40 60 80 100

time (h)

Des. 99% 7CNF++1CM
P_7CNF+/1CMC

Des. 99% 4CNF+4CM
P_4CNF+4CMC

Des. 75% 7CNF+1CM
P_4CNF+4CMC

Open porous system on top, in cross-section & on bottom
CONCLUSIONs

➢ The enzyme-mediated phosphorylation of NC was confirmed, resulting to very low SD, and inability of regeneration of very expensive ATP as well as cofactor (Mg^{2+}).

➢ Chemically-phosphorylated approach (esterification) using H_{3}PO_{4} in heterogeneous (in water) and homogeneous (in molten urea) conditions, yielding a CNF with much higher charge densities, but lower stability in highly molar (>10mM) acidic (pH<3) or alkaline (pH>8) mediums.

➢ Very stable chemical-phosphorylation of CNF via COOH groups using Apa/Aln molecule (bearing one/two phosphate group-s) was examined, showing an enlarged intrinsic adsorption potential towards positively charged molecules (e.g. cationic dyes and metals) in more alkaline region (pH > 7).

➢ New application potentials (filtration, composite, biomedical) are confirmed.