

Supplementary Information

## Modifying soluble NPK release with hydrophobized nanocellulose-based hydrogels for sustainable enhanced efficiency fertilizers

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### Method

#### *Gas-phase esterification.*

A graphic of the reaction setup is shown below in Figure S1.

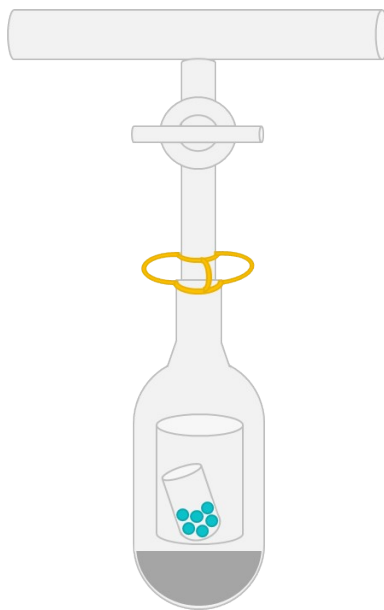


Fig. S1. Graphic of gas-phase esterification reaction, showing a custom-designed reaction vessel on a Schlenk line. The NPK-CNF beads (blue) are shown inside an inner compartment, suspended above the hexanoyl chloride (dark grey) reagent. By preventing physical contact between the solid sample and the liquid reagent, only vaporized reagent will react with the CNFs.

### *NPK release in water measured by conductivity*

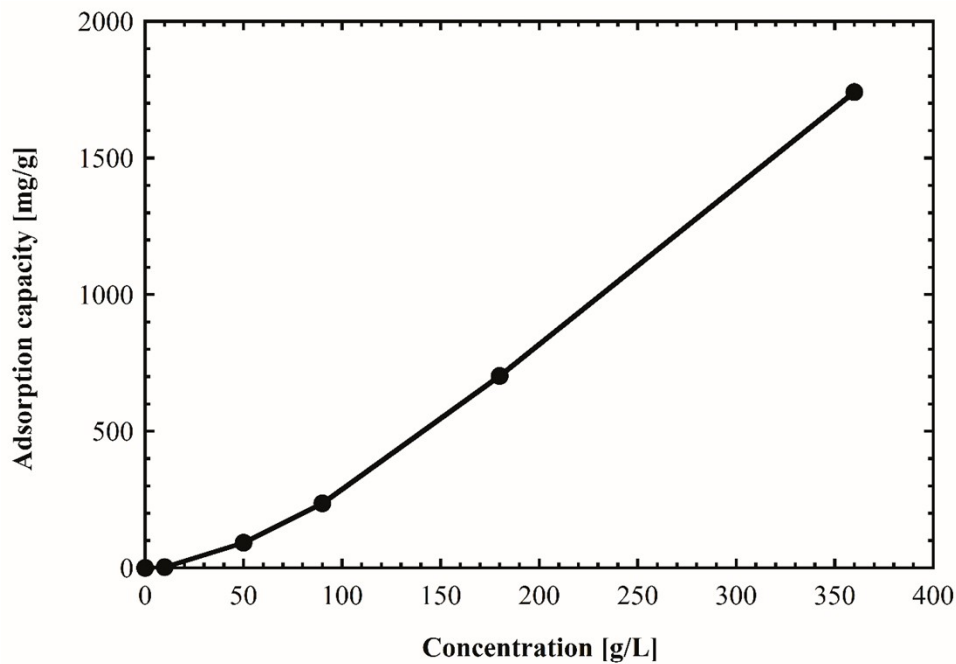
For preliminary NPK release tests in water, 0.25 g of loaded beads were placed in 100 mL of deionized water at 25 °C and stirred at 60 rpm (Fisher Sci. Electronic stirrer, 2008). The conductivity was measured at 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 180, and 240 minutes using a Symphony B30PCL pH and EC meter. Each material was measured in triplicate. For converting the conductivity to NPK release, a standard curve was generated using different NPK concentrations dissolved in ultrapure water from 0.01 to 0.4 g, resulting in a linear equation with an adjusted correlation coefficient of 0.9777. Statistical analysis was done in Statistical Analysis System (SAS) software (SAS Institute, USA) using a Tukey test to compare data sets.

### *Energy Dispersive Spectroscopy (EDS) Analysis*

EDS spectra were taken using a Helios G5 UC DualBeam scanning electron microscope (SEM) equipped with an EDAX Octane Elite EDS system. All EDS measurements were replicated over at least 2 areas and on multiple beads. Peaks were assigned manually based on known species present in the sample.

## **Results**

### *Characterization and loading of NPK-CNFs*



*Fig. S2. Adsorption capacity of the washed beads after 72 hours of immersion in fertilizer solutions.*

Table S1. Solid content of the loaded materials and fertilizer calculations

Fertilizer concentration	Wet weight	Dry Weight	Expected weight	Moisture content	Solid content	Extra solid content	calculated mg of fertilizer	Difference of expected and dry weight	Percent of fertilizer in solid
[%]	[mg]	[mg]	[mg]	[%]	[%]	[%]	[%]	[mg]	[%]
Washed	538.6	14		97.40	2.60	0.00	0.00	N/A	N/A
Unwashed	214.9 ± 96.6	20.0 ± 6.8	5.6 ± 2.2	90.8 ± 0.6	9.21 ± 0.6	6.6 ± 0.4	1.14 ± 0.6	12.2 ± 6.4	71.8 ± 1.3
1	170.4 ± 13.2	7.75 ± 20.2	5.5 ± 0.3	95.5 ± 0.1	4.6 ± 0.1	1.9 ± 0.1	0.15 ± 0.0	2.21 ± 0.2	28.6 ± 0.6
5	177.6 ± 6.2	12.2 ± 20.6	5.5 ± 0.4	93.1 ± 0.2	6.9 ± 0.2	4.27 ± 0.2	0.52 ± 0.01	6.71 ± 0.6	55 ± 3.4
9	164 ± 53.6	16.2 ± 21.1	5.7 ± 0.5	89.9 ± 0.9	10.0 ± 0.9	7.4 ± 0.9	1.18 ± 0.2	10.53 ± 4.5	63.5 ± 12.3
18	169.6 ± 30	20.0 ± 22.0	5.8 ± 0.4	88.1 ± 1.2	11.9 ± 1.3	9.3 ± 1.2	1.86 ± 0.1	14.3 ± 1.1	71.3 ± 0.1
36	3401.9 ± 500.1	1062.4 ± 177.4	130.8 ± 1.4	68.9 ± 0.8	31.2 ± 0.8	28.6 ± 1.2	304.3 ± 58.1	931.7 ± 177.5	87.5 ± 1.9
Super-saturated	3205.7 ± 120.4	1896.83 ± 63.4	84.8 241 0.2	40.8 ± 0.3	59.2 ± 0.3	56.4 ± 0.0	1073.1 ± 31.7	1812.0 ± 63.5	95.5 ± 0.2

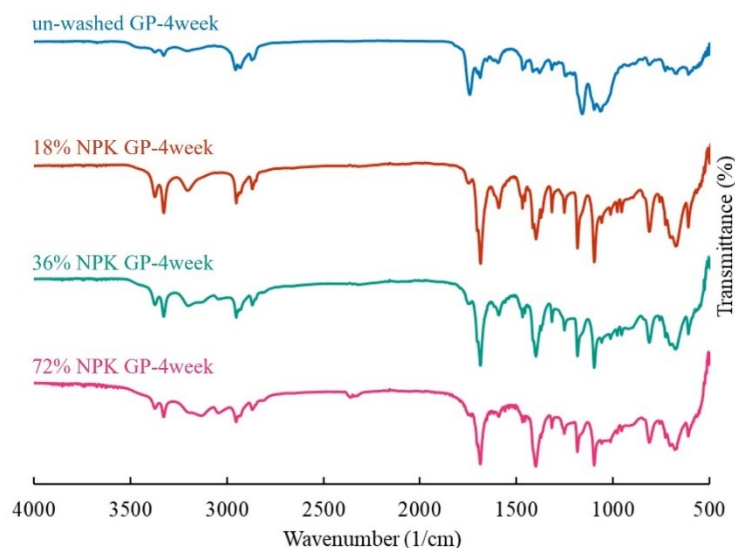


Fig. S3. ATR-FTIR spectra for gas-phase (GP) esterified NPK-CNFs, at loadings of 0, 18, 36, and 72% NPK.

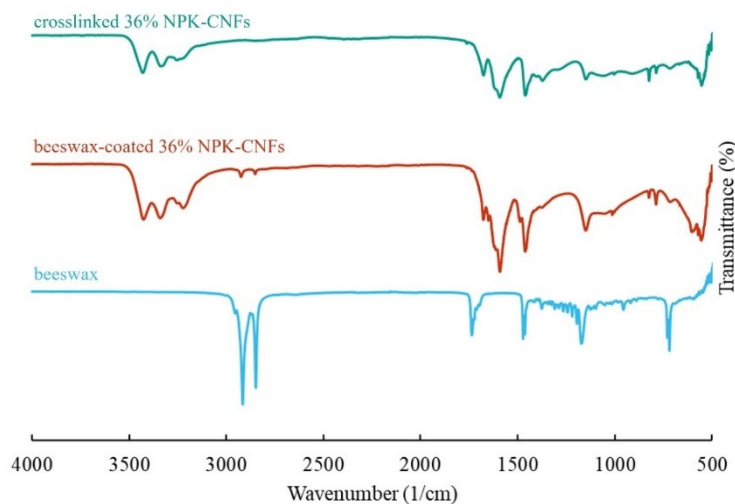
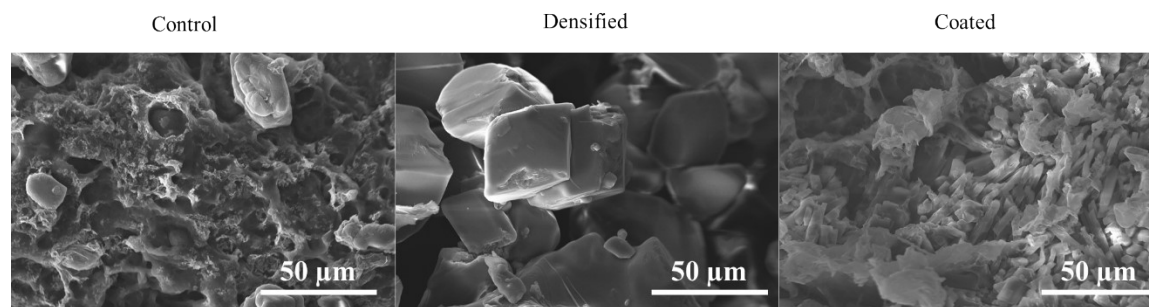
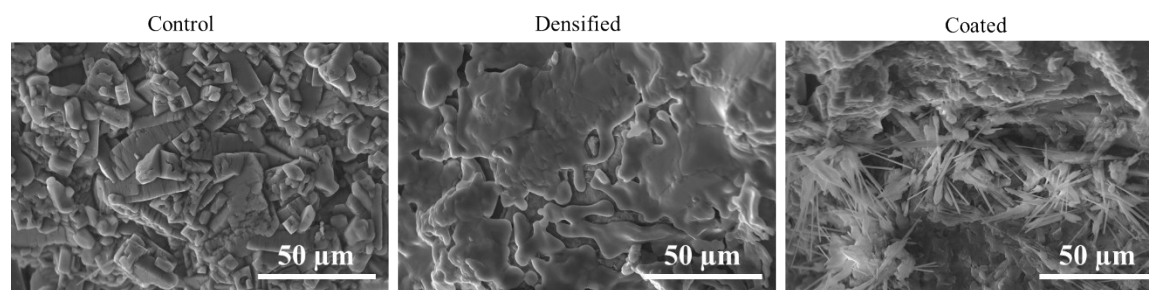


Fig. S4. ATR-FTIR spectra of 36% NPK-CNFs crosslinked and densified with maleic anhydride, 36% NPK-CNFs coated with beeswax, and the beeswax used for coating.

Densification with maleic anhydride was supported by the absence of a wide hydroxyl stretching band ( $3600 - 3100 \text{ cm}^{-1}$ ), as these groups were consumed in the reaction. Only amine groups from residual urea are visible in this region. Additionally, a new band appeared around  $1230 \text{ cm}^{-1}$  due to cyclic anhydride C-O-C stretching.<sup>1</sup> The beads coated with beeswax displayed the C-H stretching ( $2850 - 2910 \text{ cm}^{-1}$ ) from the pure beeswax as seen in Fig. S4, as well as its carboxyl groups around  $1715 \text{ cm}^{-1}$ , demonstrating the addition of the beeswax to the surface of the beads. These changes were maintained even in the loaded solutions.



*Fig. S5. SEM images of the unmodified, un-loaded CNF beads: the unmodified control (left), densified with maleic anhydride (middle), and coated with beeswax (right).*



*Fig. S6. SEM images of the unmodified, 36% NPK-loaded beads: the unmodified control (left), densified with maleic anhydride (middle), and coated with beeswax (right).*

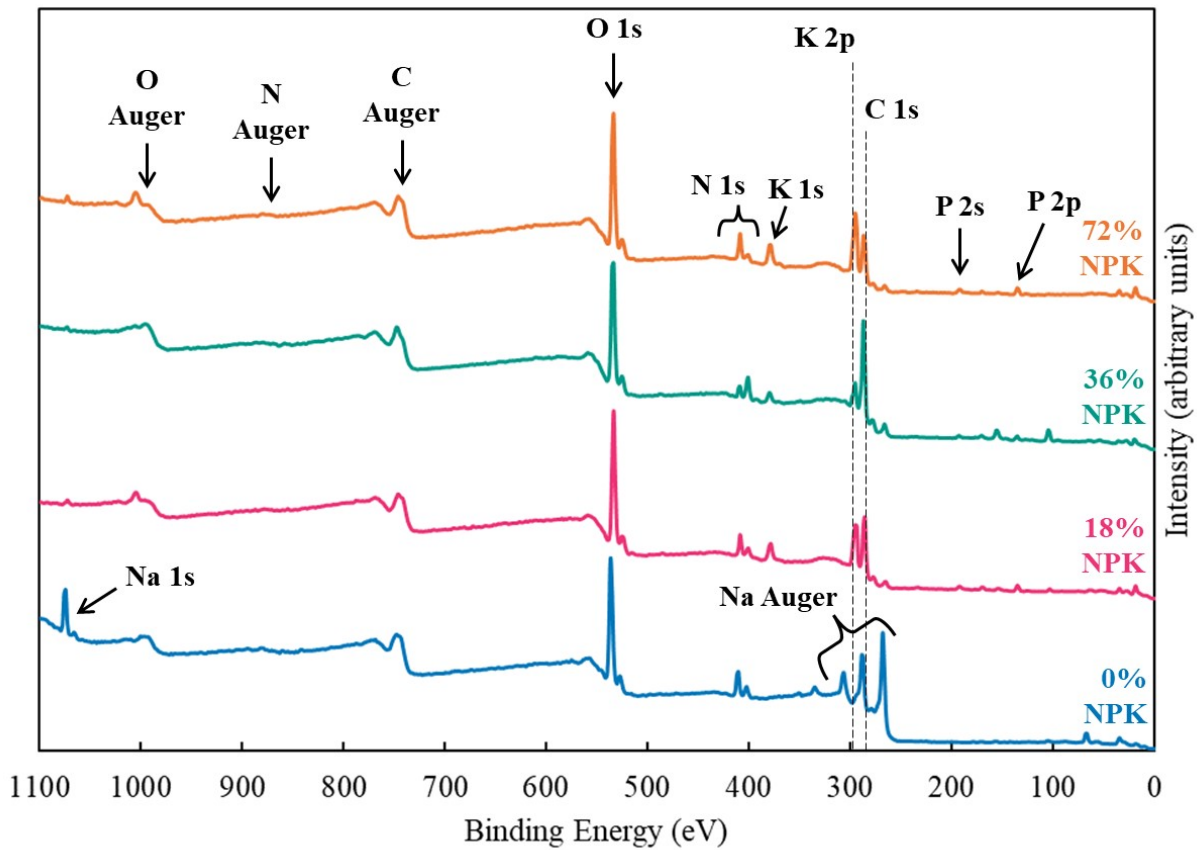


Fig. S7. XPS survey spectra of unmodified NPK-CNF beads after immersion in varied concentrations of NPK-rich fertilizer solution and drying. These spectra indicate the presence of carbon, nitrogen, and oxygen in all samples. The unloaded, un-washed 0% CNFs also contain notable sodium, while the 18, 36, and 72%-loaded CNFs contain additional phosphorus and potassium. Spectra were normalized to the intensity of the O 1s peak.

## Characterization of CNFs after release of NPK

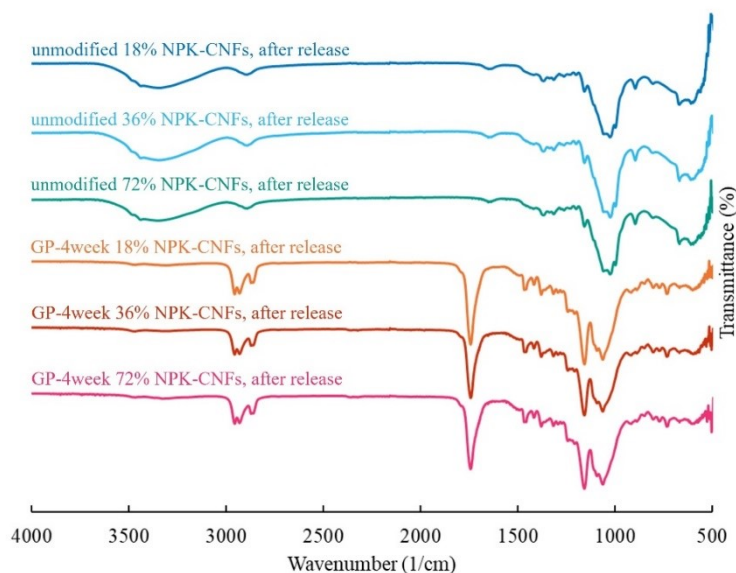


Fig. S8. ATR-FTIR spectra for both unmodified and gas-phase (GP) esterified NPK-CNFs at loadings of 18, 36, and 72%, after complete release of NPK.

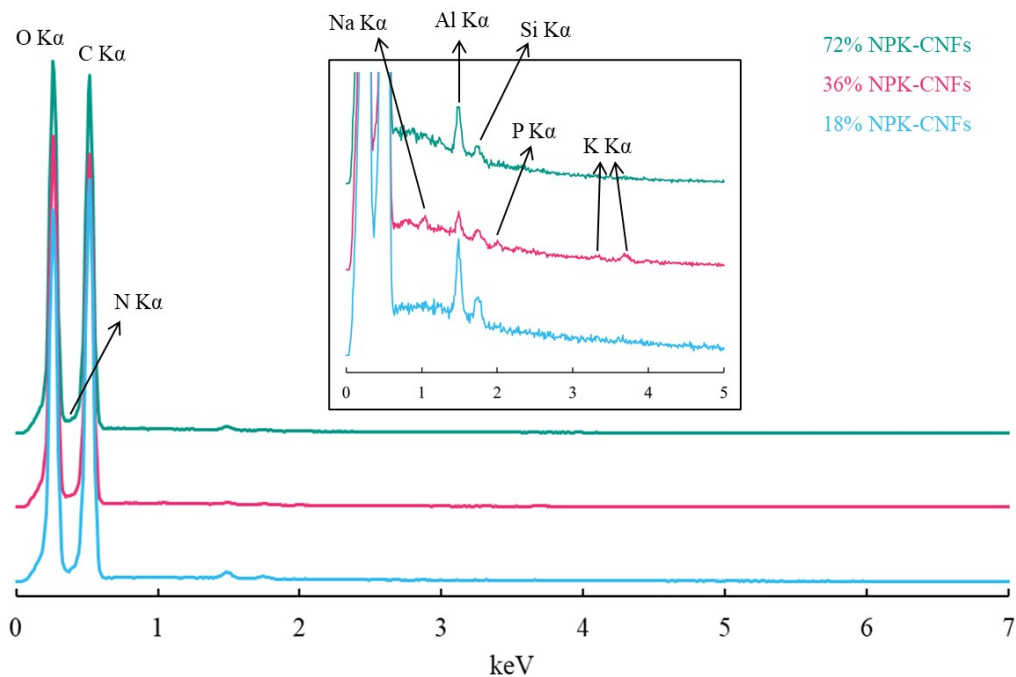
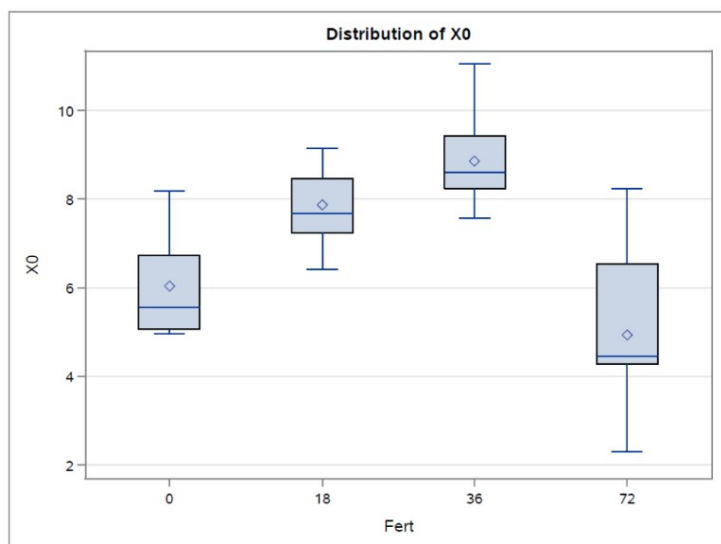


Fig. S9. SEM-EDS spectra of 72, 36, and 18% NPK-CNFs after aqueous release of NPK. The insert shows the low-count peaks between 0 and 5 keV.

EDS shows that all NPK-released CNF samples contain primarily oxygen and carbon, as expected. Due to the significantly high intensity of the C and O K $\alpha$  peaks, the N K $\alpha$  peak that appears between them is

obscured and cannot reasonably be quantified. Due to the low abundance of elements other than C and O, elemental abundance was not calculated for these samples. The small aluminum  $K\alpha$  peak found in all samples results from scattering by the aluminum sample holder, while the silicon  $K\alpha$  peak is a likely contaminant from the un-purified raw feedstock. In 18 and 72% NPK-CNF samples, no visible phosphorus or potassium peaks can be observed above the noise level. However, the 36% sample shows some trace P and K at a very low abundance, which further supports the slowed release profiles obtained for this loading percentage. The 36% sample also contains a small amount of sodium, which likely originates from the sodium hydroxide used in the regeneration process. Overall, these spectra confirm removal of all but trace levels of P and K from these samples, indicating that the measured ICP-OES profiles capture the entire release process.

*NPK release in water measured by conductivity*



Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Fert
A	8.8658	9	36
A			
A	7.8748	9	18
B	6.0466	9	0
B			
B	4.9464	9	72

*Fig. S10. Statistical comparison of the release measured in water by the changes of conductivity of the unmodified systems. X0 indicates the time required for a stable conductivity reading.*



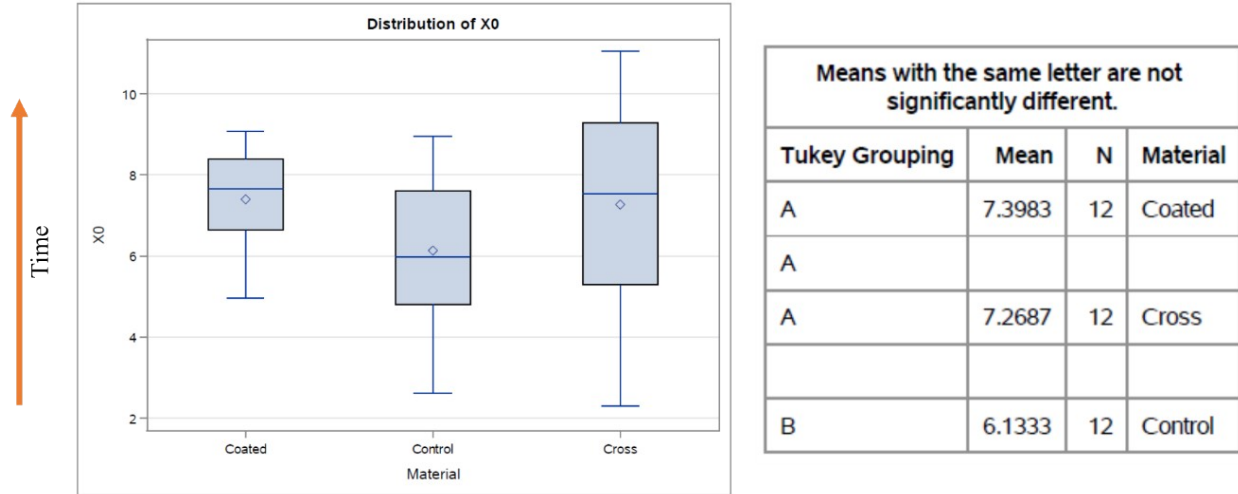


Fig. S11. Statistical comparison of the release in water measured by conductivity profiles in ultrapure water. Here “Cross” corresponds to the densified beads, and “Control” to the loaded but unmodified beads. X0 indicates the time required for a stable conductivity reading.

*NPK release in water measured by ICP-OES*

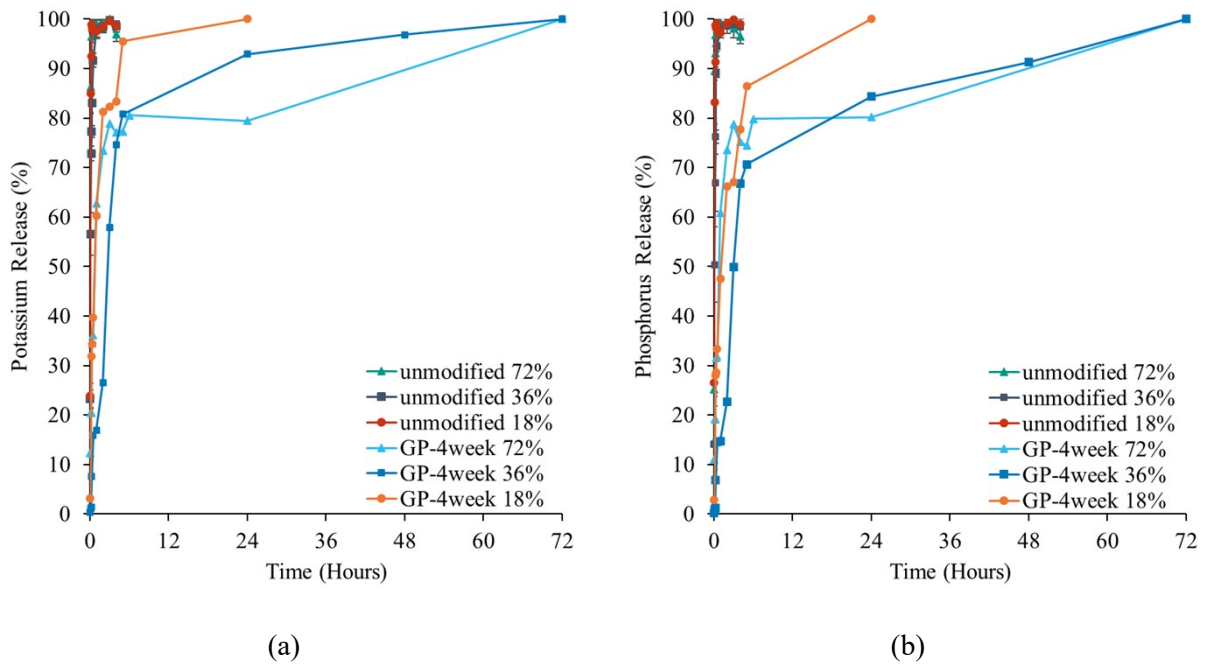


Fig. S12. ICP-OES data showing the release of potassium (left) and phosphorus (right) from unmodified and gas phase esterified (denoted GP) NPK-CNFs at 18, 36, and 72% loading of NPK, plotted up to 72 hours.

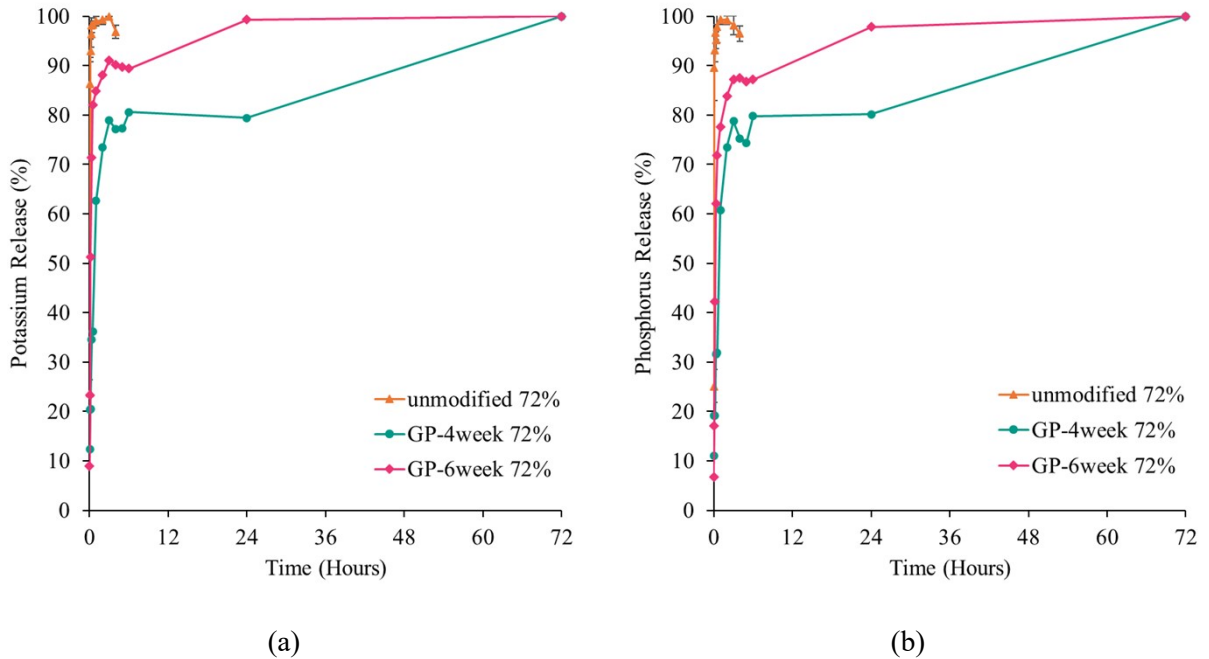


Fig. S13. ICP-OES data for unmodified NPK-CNFs (triangles) and samples that were gas-phase (GP) esterified for 4 (circles) and 6 (diamonds) weeks, all at 72% loading of NPK, plotted up to 72 hours.

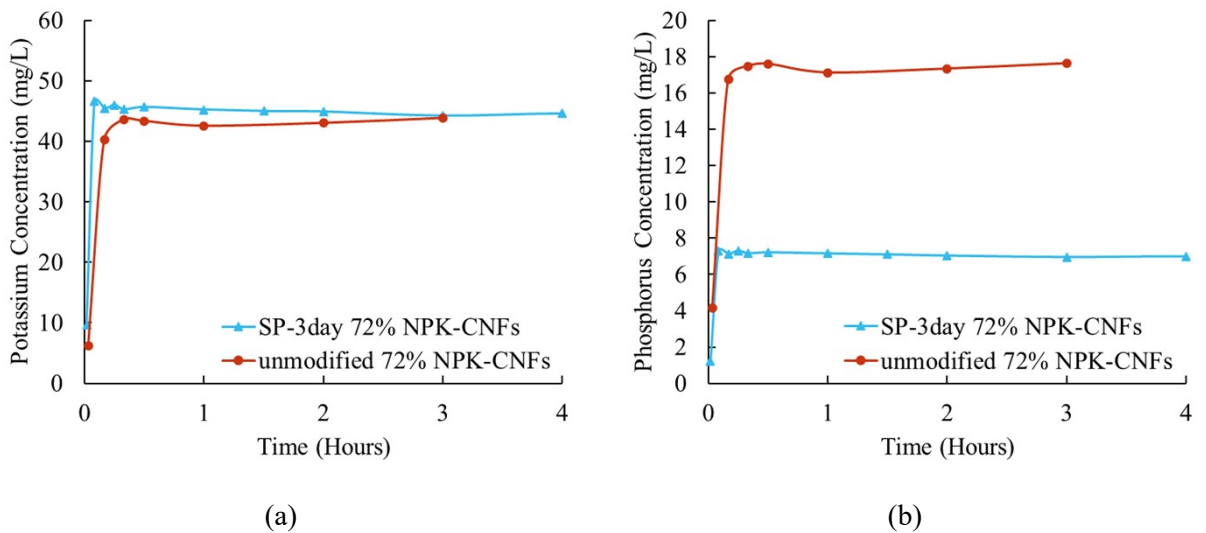
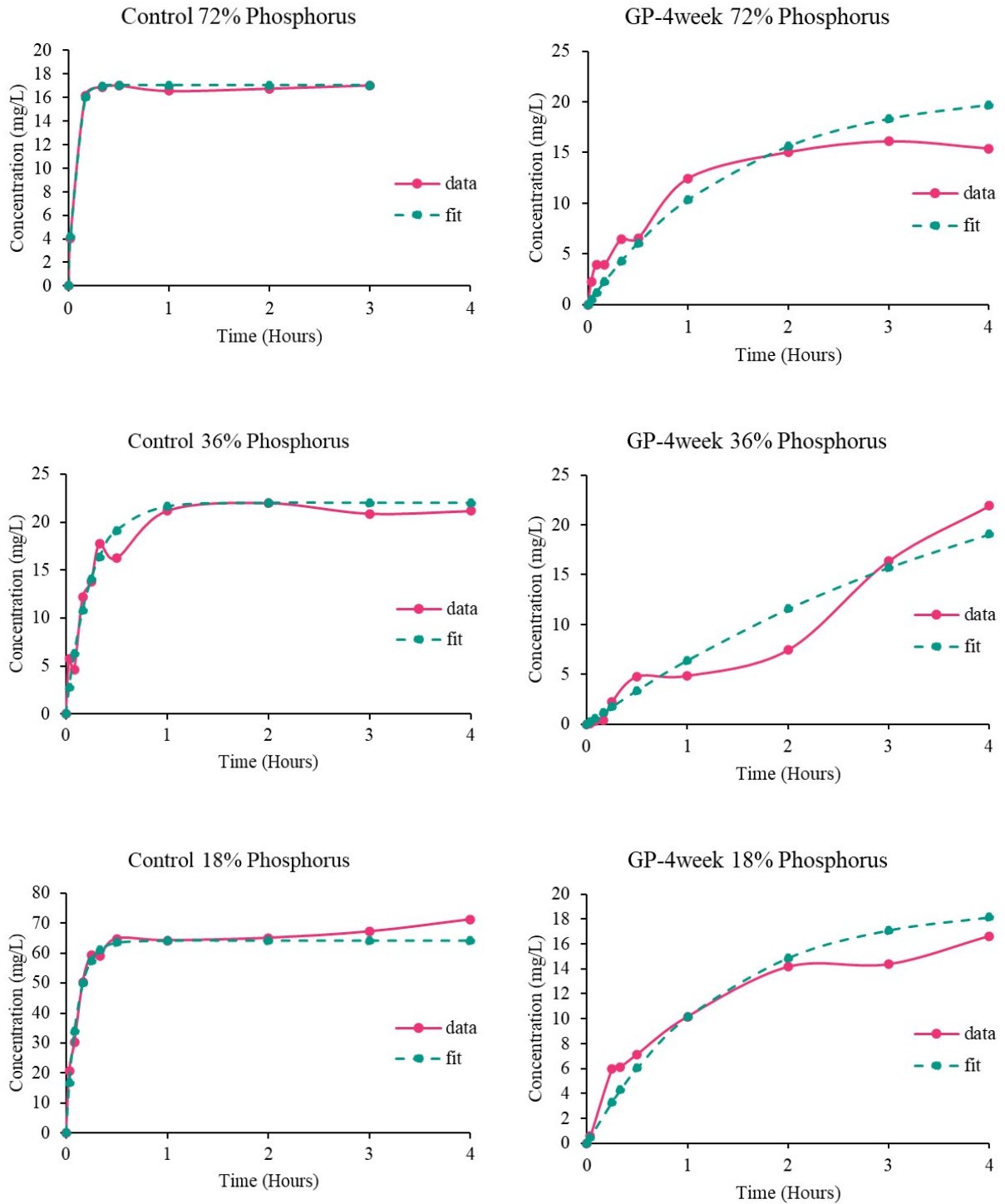


Fig. S14. Release profiles of potassium (left) and phosphorus (right) for unmodified (circles) and solution-phase (SP) esterified (triangles) 72% NPK-CNFs, plotted in terms of concentration.

As Fig. S14 shows, the solution-phase esterification was ineffective at extending the release of NPK from the nanocellulose matrix. In fact, dissolution occurred more rapidly from the esterified matrix than the unmodified control; NPK released completely in 5 minutes with the SP-esterified sample, compared to 30 minutes for the unmodified control. In addition, a dramatic reduction in phosphorus content was observed upon solution-phase modification, representing significant material waste and greatly reducing the nutrient

loading of the CNF matrix. Overall, the solution-phase modification was found to be unsuccessful in this application.

*Kinetic fitting of ICP-OES release data*



*Fig. S15. Experimentally determined (solid line) and mathematically derived (dashed line) profiles for the release of phosphorus from ICP-OES data. Data was fit to a first order rate law equation.*

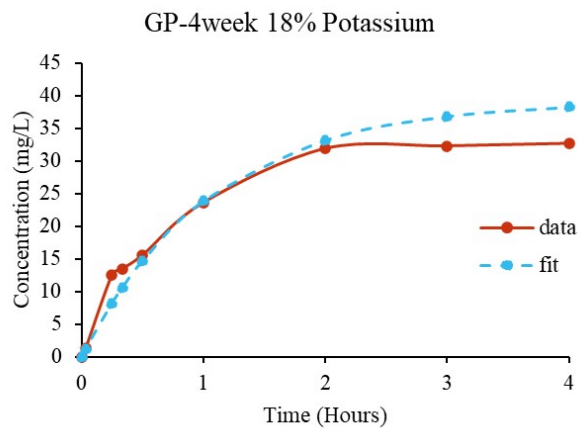
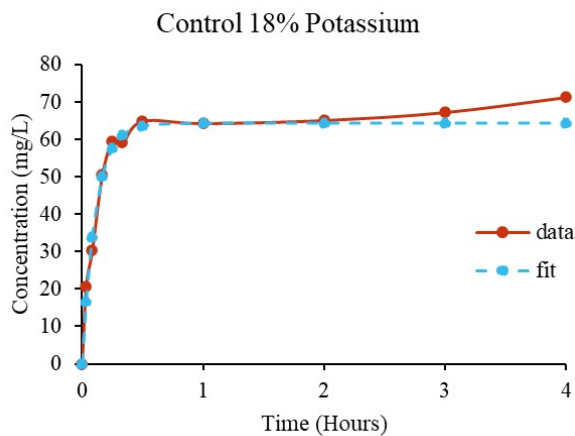
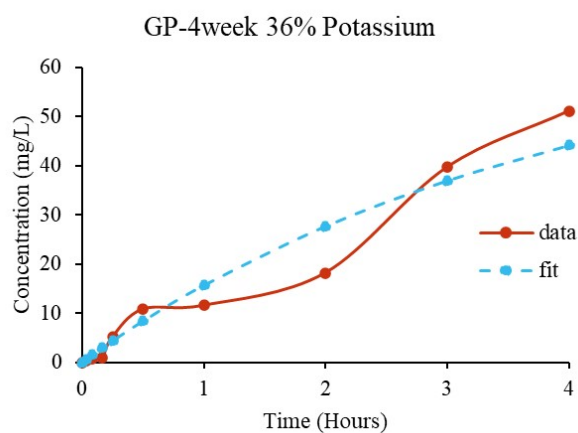
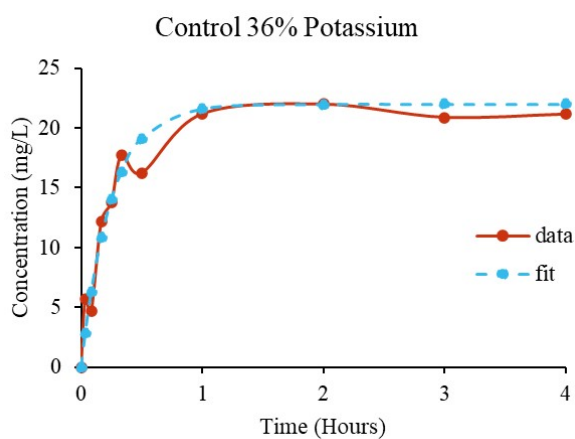
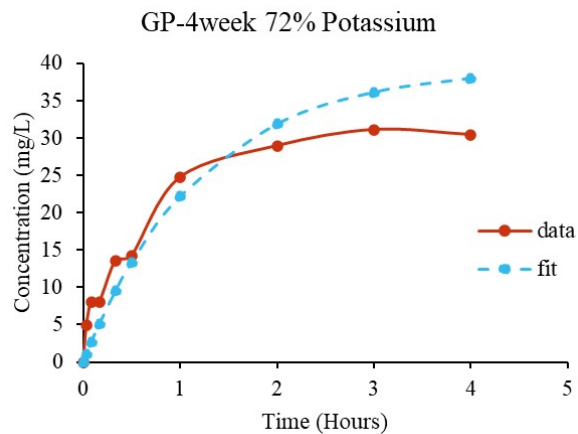
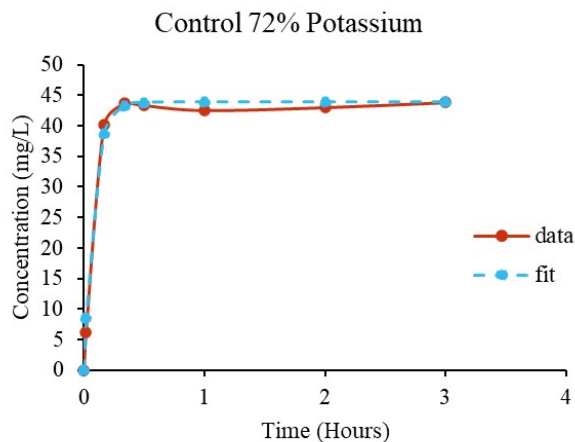


Fig. S16. Experimentally determined (solid line) and mathematically derived (dashed line) profiles for the release of potassium from ICP-OES data. Data was fit to a first order rate law equation.

## **Additional References**

1. X. Gu and C. Q. Yang, FT-IR and FT-Raman spectroscopy study of the cyclic anhydride intermediates for esterification of cellulose: I. Formation of anhydrides without a catalyst, *Research on chemical intermediates*, 1998, **24**, 979-996.