Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information

Humic acid adsorption onto cationic cellulose nanofibers for bioinspired removal of copper (II) and a positively charged dye

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S1 : FTIR spectra of CNF

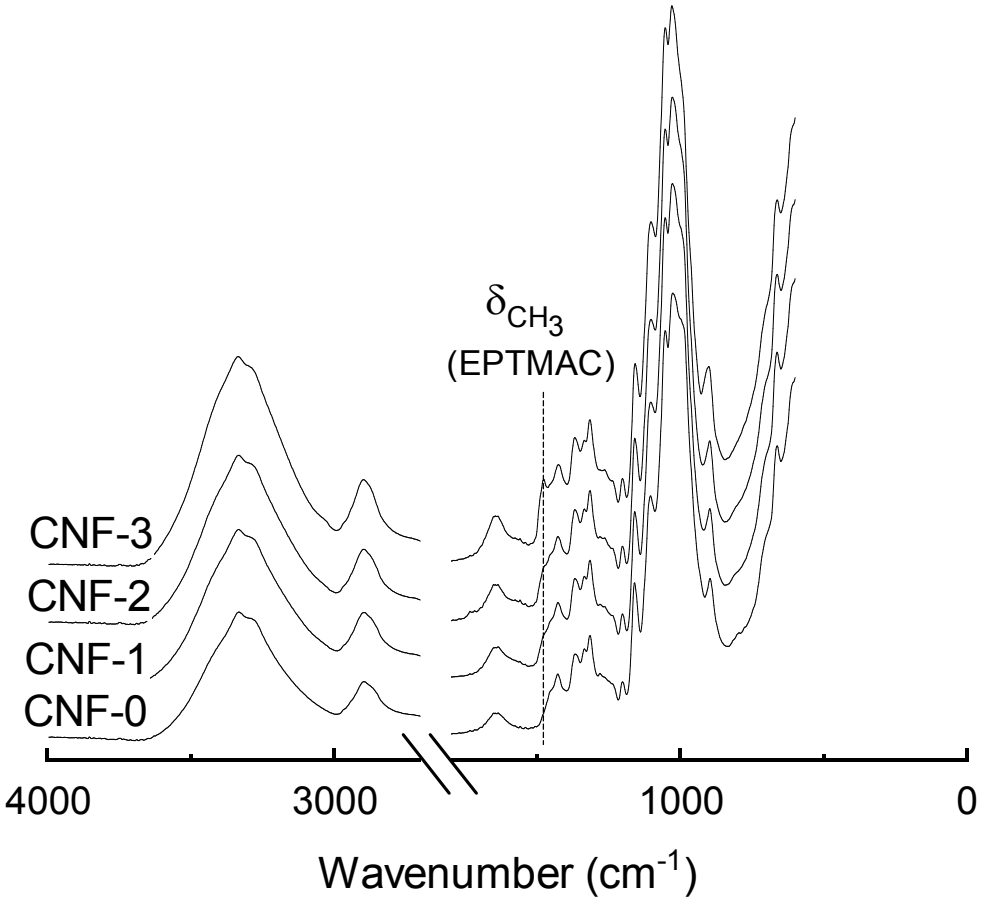


Figure 1 : FTIR spectra of unmodified nanofibers (CNF-0) and cationic nanofibers (CNF-1; CNF-2; CNF-3). A peak corresponding to the bending vibration of the methyl moieties of the quaternary ammonium groups could be seen for CNF-3 while a shoulder is observed for CNF-1 and CNF-2.

SI2 : Titration curves for cationic CNF

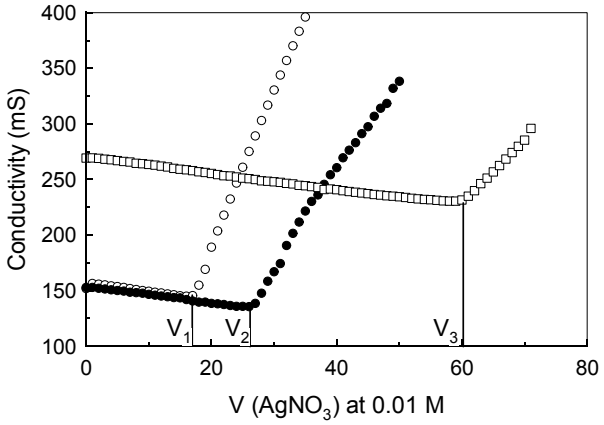


Figure 2 : Conductometric titration of ammonium groups in cationic nanofibers. V_1, V_2 and V_3 correspond to the volume of silver nitrate needed to titrate 0.5 g of CNF_1, CNF_2 and CNF_3, respectively.

SI 3: Modelling of the adsorption equilibrium data using Langmuir and Freundlich equations

Langmuir model is based on a monolayer adsorption onto a surface. The Langmuir equation is given by:

$$\frac{X}{X_{\max}} = \frac{bC}{1+bC}$$

Where X is the amount of humic acid adsorbed per unit weight of CNF at equilibrium concentration (mg/g), C is the equilibrium concentration of the humic acid solution (mg/L), X_{max} is the maximum amount of adsorption at monolayer coverage (mg/g), and b is the adsorption equilibrium constant. This equation can be written as:

$$\frac{1}{X} = \frac{1}{X_{\max}} + \frac{1}{X_{\max}}\frac{1}{bC}$$

A plot of 1/X versus 1/C would generate a straight line when the adsorption process follows Langmuir model.

Freundlich model supposes a heterogeneous adsorption mechanism and its equation is:

$$X = P.C^{1/n}$$

This equation is equivalent to: $\log X = \frac{1}{n}\log C + \log P$

A plot of log X versus log C would generate a straight line when the adsorption process follows Freundlich model.

Experimental data were curve fitted using Langmuir and Freundlich models, and the coefficients of determination (R^2) were obtained from both models. Results are represented in the table below.

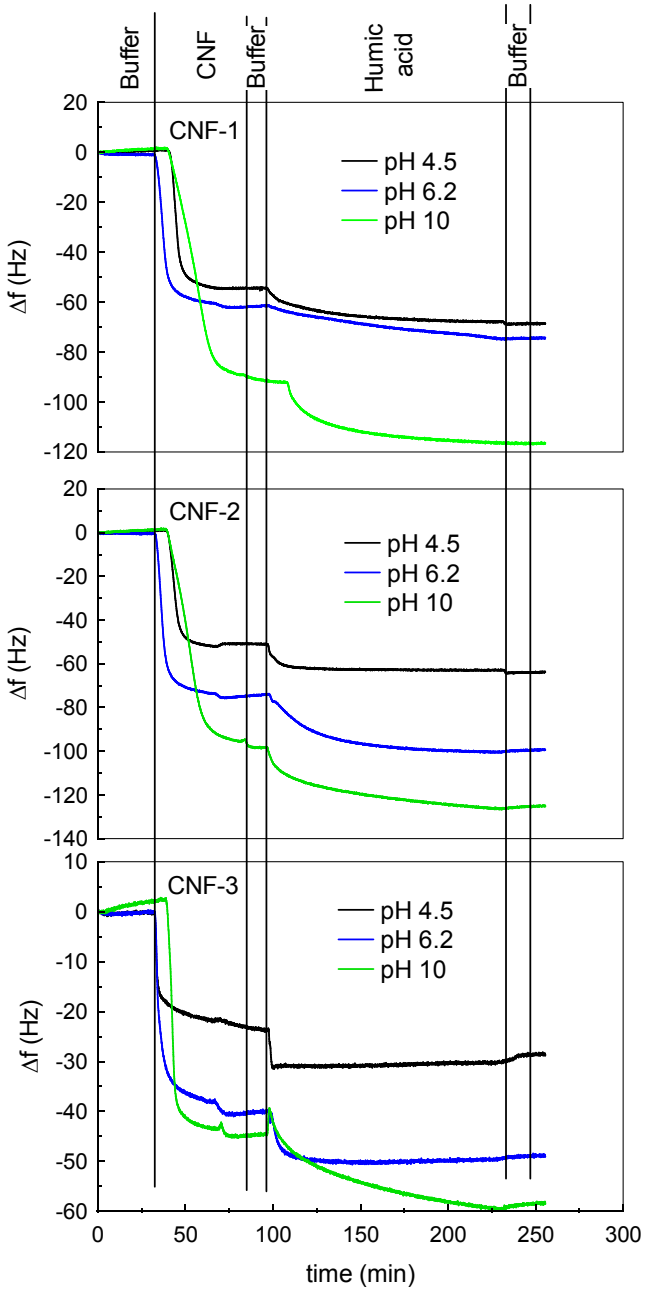
	CNF-1	CNF-2	CNF-3
R^2 for equation curve fitting Freundlich	0.926	0.925	0.948
R^2 for Langmuir equation curve fitting	0.969	0.987	0.986

Since R^2 for Langmuir model is closer to 1 than those for Freundlich model, it is expected that the adsorption process is better represented by a monolayer adsorption of HA onto the CNF.

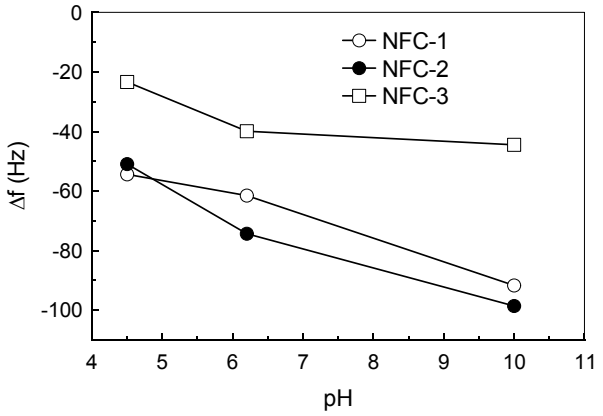
SI 4: Scheme representing the adsorption process of humic acid onto cationic CNF at low and high pH

At low pH, humic acid adopt a coiled conformation, and therefore a larger number of molecules can adsorb onto cationic CNF. At high pH, the conformation of humic acid is rather linear leading to fewer molecules and thinner layer of humic acid adsorbed as compared to the case at high pH.

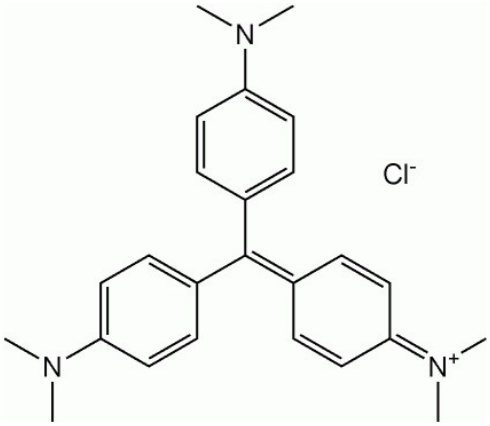
SI 5: QCM-D frequency shift curves corresponding to the third overtone



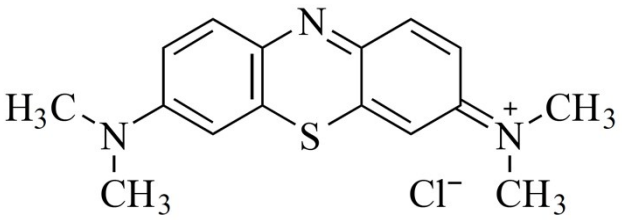
SI 6: Frequency shift at equilibrium due to the adsorption of different CNF's on the silica sensor. These frequency shifts correspond to the third overtone



SI 7: Chemical structure of crystal violet and methylene blue adsorbed onto cationic CNF-1/HA complex

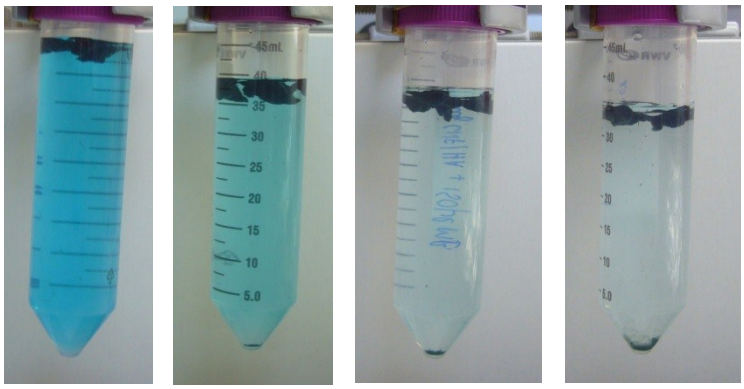


Crystal vilet



Methylene blue

Color lightning upon exposure time due to methylene blue uptake by the CNF-1/HA foam.



t=0h t=4h t=24h t=48h