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:

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

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), $X_{\text{max}}$ is the maximum amount of adsorption at monolayer coverage (mg/g), and $b$ is the adsorption equilibrium constant.

This equation can be written as:

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

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.

<table>
<thead>
<tr>
<th></th>
<th>CNF-1</th>
<th>CNF-2</th>
<th>CNF-3</th>
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<tr>
<td>$R^2$ for equation</td>
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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

![Graph showing frequency shift vs. pH for different CNF samples.]

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

![Chemical structures of Crystal violet and Methylene blue.]

Crystal violet

Methylene blue

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

![Images showing color change over time.]

$t=0\text{h}$  $t=4\text{h}$  $t=24\text{h}$  $t=48\text{h}$