

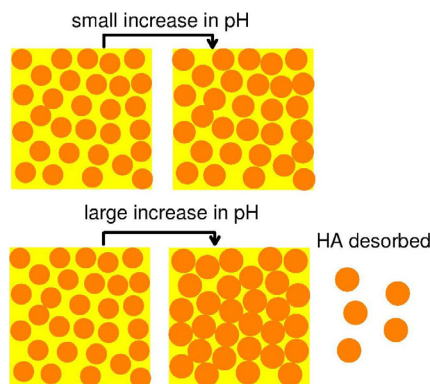


## Regular Article

## Humic acid desorption from a positively charged nanocellulose surface

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Trimethyl-ammonium functionalized cellulose nanofibers (CNF) display a positively charged surface over a wide pH and ionic strength range, and constitute therefore not only an interesting biobased sorbent material, but also a positively charged model surface to investigate sorption phenomena. In the current work, CNF were totally or partially covered by humic acid (HA) at pH ~6, and the desorption process of HA from CNF was thereafter studied in batch and continuous filtration experiments at various pH and ionic strength. It is found that the desorbed amount of HA increases and the kinetic of desorption is faster via increasing the pH and ionic strength of the solution. Moreover, the desorption is affected by the extent of CNF coverage with HA and by the presence of free HA in solution. The present work gives insights into the interaction of HA with permanently positively charged surfaces and was successfully exploited for the removal of HA from CNF filters for regeneration allowing multiple filter utilization.

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## 1. Introduction

Humic acid (HA) belongs to humic substances, i.e., organic matter present in soils and natural waters coming from the decomposition of plants and animal residues. HA comprises in its structure functional carboxylic and phenolic moieties conferring it a net

negative charge in natural waters. In the environment, HA develops specific and electrostatic interactions with other soil components and with a number of entering pollutants such as pesticides, heavy metal ions, viruses and nanoparticles [1–10]. Hence, HA interaction with various organic and inorganic substances has been extensively studied in environmental science, because it is related to the fate and transport of pollutants into natural environments. In the field of water treatment, such interaction aimed at studying membrane fouling or at developing an

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economical HA sorbent to counteract undesirable presence of HA in drinking water [11–18].

Unlike the adsorption process of HA that has been widely explored, its desorption process has encountered far less interest despite its critical importance in environmental, soil and water sciences. Most studies dealt with HA desorption from iron oxide surface (as an important soil component) and came to the conclusion that soil organic matter, once adsorbed to iron oxide, is very difficult to desorb only by dilution (i.e. decreasing HA concentration), whereas increasing pH with or without changing HA concentration in solution lead to a considerable and fast HA desorption [19–21]. Furthermore, there is a surface charge reversal of iron oxide upon pH change and this affects electrostatic adsorption/desorption of HA [2].

In our previous work, we have shown that cellulose nanofibers functionalized with trimethyl ammonium functions (CNF) have a large specific surface area and a positive surface charge over a wide pH range, making it a good HA sorbent in acidic and basic pH registering a maximum adsorption capacity as high as 310 mg of HA per gram of nanofibers [17]. CNF processing into porous filters permitted HA removal from aqueous solution via filtration [18]. Effective utilization of CNF filters for HA removal requires filter regeneration, i.e. desorption of HA from CNF. Hence, a good understanding on parameters affecting HA structure and its interaction with positively charged surfaces is relevant for practical applications.

In the present work, cationic CNF were prepared and characterized in terms of their morphology, surface charge, and HA adsorption properties. CNF with 3 different loadings of HA were thereafter subjected to HCl, NaOH or NaCl solutions and the desorption process was studied in batch experiments. Furthermore, we produced porous filters from CNF which were used in filtration experiments for HA removal by adsorption. Subsequently, we investigated the reversibility of the adsorption process, as well as the kinetic and extent of HA desorption from the filter. Possible mechanisms occurring during the desorption process are discussed.

## 2. Materials and method

Pulp residue, a waste product from pulp and paper industry with a cellulose and hemicellulose content of 95% and 4.75%, respectively, was kindly provided by Processum AB, Sweden [22]. 2,3-epoxypropyl trimethyl ammonium chloride (EPTMAC), and humic acid were purchased from Sigma Aldrich.

### 2.1. CNF preparation

Cationic CNF were prepared according to a method reported by Pei et al. by using 1.25 mL of EPTMAC per gram of the pulp, and conducting the reaction at 80 °C for 8 h [17,23,24]. The ammonium group content of the cationic CNF is 0.37 mmol g<sup>-1</sup> as determined by conductometric titration of chloride ions using AgNO<sub>3</sub> [25].

HA stock solution was prepared as reported elsewhere [17,18], by dissolving HA in water at a concentration of 1 g L<sup>-1</sup>, and purifying it by pre-filtration through a 0.65 μm membrane (DVPP, millipore). HA concentrations were measured with a UV-vis spectrophotometer (Spectronic Camspec Ltd., UK) at 254 nm by constructing calibration curves beforehand.

ζ-potential measurements were performed on solutions at ~0.1 wt% using a Zetasizer NanoZS instrument (Malvern, UK) by monitoring the electrophoretic mobility. TEM investigations were carried out on a JEOL 2200 FS at 200 kV, using plasma-treated copper grids and staining CNF with methylamine Vanadate solution (NanoVan).

### 2.2. HA adsorption in batch experiments

Adsorption isotherm of HA onto CNF were conducted as reported elsewhere [17]. To obtain CNF with three different surface coverage by HA, 1 g dry weight of CNF was mixed for 48 h at 150 rpm (Ika HS 260) with 50, 100 or 250 mg of HA at a total volume of 1.2 L. Unbound HA was removed via a series of centrifugation (20 min at 5000 rpm), supernatant removal, and fresh milli-Q water addition. The concentrations of HA in the supernatants was determined giving the amount of HA adsorbed to CNF.

### 2.3. HA desorption in batch experiments

After washing by centrifugation, NaCl, NaOH or HCl solution was added to 28 mg of CNF containing adsorbed HA and the total volume was set to 45 ml. The mixture was shaken for 48 h at 150 rpm (Ika HS 260), and then centrifuged at 5000 rpm for 20 min. The concentration of HA in the supernatant was thereafter measured giving the amount of HA desorbed from CNF.

During desorption, free humic acid (not bound to CNF) is generated, which itself may influence further the desorption process. To investigate the effect of free HA concentration (i.e. effect of desorbed HA concentration) on desorption, various amounts of CNF with adsorbed HA of 7, 14, 28 or 56 mg were shaken for 48 h at 150 rpm with NaCl or NaOH solution while the total volume being 45 ml. The mixture was then centrifuged to determine the free HA concentration as well as the amount of HA desorbed from CNF.

### 2.4. CNF filter preparation

CNF filters with a grammage (weight per unit area) of 50 g m<sup>-2</sup> were prepared by freeze-drying as reported elsewhere [18]. CNF suspension at 0.75 wt% was first frozen at -20 °C and the ice was thereafter sublimated at low pressure (Lyovac freeze-dryer; SRK System Technik GmbH). CNF foam thus obtained was hot pressed at 105 °C for 20 min under a pressure of 2.2 bar (Carver Inc., USA) resulting in CNF filter of 76% porosity.

### 2.5. HA adsorption to and desorption from CNF filters in dynamic filtration experiments

HA adsorption onto CNF filter was realized by permeating HA solution at 250 mg L<sup>-1</sup> through CNF filter in a dead-end Sterlitech device (active filtration area is 1460 mm<sup>2</sup>, HP4750, Kent, USA) using nitrogen at a head pressure of 1 bar. HA concentration in the filtrate was measured by UV spectrophotometry giving the amount of HA adsorbed by the filter. HA desorption was obtained by elution, at 1 bar, of NaCl, NaOH or a combination of both solutions through the CNF filter containing adsorbed HA. The concentration of HA in the filtrate was determined at different time intervals thus giving the kinetic and extent of HA desorption from CNF filter. The initial desorption rate is defined as the initial slope of the graph showing the amount of HA desorbed versus time. The final desorbed amount of HA is taken at ca. 1000 min filtration. The reversibility study was conducted via three adsorption-desorption cycles wherein 1 M NaCl solution at pH 12 was eluted through CNF filter containing adsorbed HA.

## 3. Results and discussion

### 3.1. HA adsorption onto CNF

Cationic CNF morphology has been investigated by transmission electron microscopy (TEM) which shows uniform nanofibers with a width of 4 nm and a high aspect-ratio (Fig. 1a). The presence of

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