



Cationic cellulose nanofibers from waste pulp residues and their nitrate, fluoride, sulphate and phosphate adsorption properties



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ABSTRACT

Cationic cellulose nanofibers (CNF) having 3 different contents of positively charged quaternary ammonium groups have been prepared from waste pulp residues according to a water-based modification method involving first the etherification of the pulp with glycidyltrimethylammonium chloride followed by mechanical disintegration. The cationic nanofibers obtained were observed by scanning electron microscopy and the extent of the reaction was evaluated by conductometric titration, ζ -potential measurements, and thermogravimetric analyses. The cationic CNF had a maximum cationic charge content of 1.2 mmol g^{-1} and positive ζ -potential at various pH values. Sorption of negatively charged contaminants (fluoride, nitrate, phosphate and sulphate ions) and their selectivity onto cationic CNF have been evaluated. Maximum sorption of $\sim 0.6 \text{ mmol g}^{-1}$ of these ions by CNF was achieved and selectivity adsorption studies showed that cationic CNF are more selective toward multivalent ions (PO_4^{3-} and SO_4^{2-}) than monovalent ions (F^- and NO_3^-). In addition, we demonstrated that cationic CNF can be manufactured into permeable membranes capable of dynamic nitrate adsorption by utilizing a simple paper-making process.

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1. Introduction

Cellulose nanofibers (CNF) refer to long and interconnected nanofibers disintegrated from plant biomass via a mechanical disintegration treatment (Henriksson, Henriksson, Berglund, & Lindstrom, 2007; Paakko et al., 2007; Turbak, Snyder, & Sandberg, 1983; Zimmermann, Bordeanu, & Strub, 2010). The abundance, renewability and environmentally benign character of cellulose as raw material, as well as the numerous possibilities for its pretreatment, disintegration and chemical modification, have contributed to the increasing interest in CNF as building block for the development of functional materials in various fields (Klemm et al., 2011). In environmental remediation, the use of natural polymers for the removal of pollutants is highly appreciated (Karthik & Meenakshi,

2015; Lakouraj, Hasanzadeh, & Zare, 2014; Lakouraj, Mojerlou, & Zare, 2014; Mostafa, Samarkandy, & El-Sanabary, 2011; Pandi & Viswanathan, 2015; Sargin, Kaya, Arslan, Baran, & Ceter, 2015; Zare & Lakouraj, 2014). In particular, the use of CNF is advantageous due to the high specific surface area of the nanofibers (Sehaqui, Zhou, Ikkala, & Berglund, 2011) and the possibility to functionalize these surfaces (Habibi, 2014; Tingaut, Zimmermann, & Sebe, 2012) allowing CNF to interact with specific contaminants. Examples of the use of functionalized CNF in environmental related applications include removal of heavy metal ions (Liu et al., 2013; Sehaqui et al., 2014), natural organic matter (Sehaqui, Perez de Larraya, Tingaut, & Zimmermann, 2015), dyes (Ma, Burger, Hsiao, & Chu, 2012; Pei, Butchosa, Berglund, & Zhou, 2013), bacteria and viruses (Ma, Burger, et al., 2012; Sato, Wang, Ma, Hsiao, & Chu, 2011), selective oil recovery from oil–water mixtures (Cervin, Aulin, Larsson, & Wagberg, 2012; Korhonen, Kettunen, Ras, & Ikkala, 2011; Zhang, Sèbe, Rentsch, Zimmermann, & Tingaut, 2014) and direct CO_2 capture from ambient air (Gebald, Wurzbacher, Borgschulte,

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Table 1
Ammonium content and substitution degree of various CNF.

	N ⁺ content (mmol g ⁻¹)	Substitution degree
CNF-1	0.34	0.06
CNF-2	0.54	0.09
CNF-3	1.2	0.19

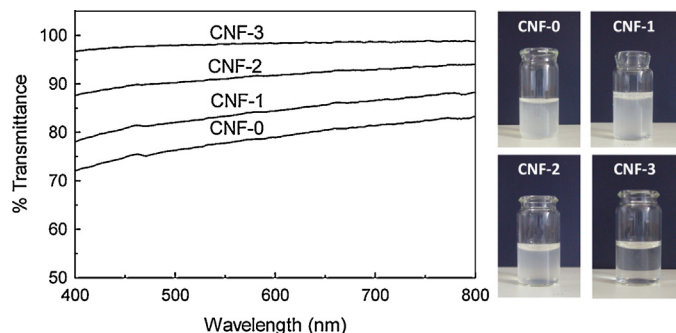


Fig. 1. UV–Vis spectra of unmodified and cationic CNF suspensions having a concentration of 0.1%.

Zimmermann, & Steinfeld, 2014; Gebald, Wurzbacher, Tingaut, & Steinfeld, 2013; Gebald, Wurzbacher, Tingaut, Zimmermann, & Steinfeld, 2011; Sehaqui, Gálvez, et al. 2015).

While different studies have highlighted the removal of positively charged contaminants in water using functionalized CNF (Ma, Burger, et al., 2012; Ma, Hsiao, & Chu, 2012; Sehaqui et al., 2014), negatively charged ions (e.g., from rocks or industrial waters) are part of the contaminants for which research should be now emphasized. For example, nitrates (NO_3^-) – emanating from the excessive use of fertilizers – and fluoride – coming from the slow natural degradation of fluorine contained in rocks or from industrial wastes – represent a potential risk to the environment and public health at higher concentration in drinking water (Ahlgren et al., 2008; Amini et al., 2008; Wolfe & Patz, 2002). Furthermore, the excess of phosphate, sulphate and nitrate present in wastewater is one of the main causes of eutrophication that affects many natural water bodies (Ahlgren et al., 2008; Boujelben et al., 2008). For these reasons, evaluating the potential of CNF for the removal of these ions may provide a readily available and inexpensive alternative to nowadays used activated carbon sorbents for wastewater treatment. Moreover, very few studies have investigated the selective removal of negatively charged ions with CNF in presence of a mixture of such contaminants.

Surface functionalization of CNF with quaternary ammonium salts (QAS) may constitute a suitable route for subsequent adsorption of negatively charged contaminants due to the permanent positive charge of QAS making them efficient anion exchangers (Hasani, Cranston, Westman, & Gray, 2008; Pei et al., 2013; Sehaqui, Perez de Larraya, et al., 2015). Modification of CNF with QAS has some advantages as it can be performed in aqueous media with the possibility to synthesize the QAS in situ in presence of cellulose prior to reaction (Gangneux, Wattiez, & Marechal, 1976). So far, quaternary ammonium modified CNF have been reported for the removal of anionic dyes (Pei et al., 2013) and natural organic matter (Sehaqui, Perez de Larraya, et al., 2015) and for the preparation of hybrid clay composites (Ho, Zimmermann, Ohr, & Caseri, 2012).

The aim of this work is to use a waste material generated from pulp and paper industry for the preparation of cationic CNF intended for the uptake of negatively charged ions. First, we report the preparation and characterization of cationic CNF, and we subsequently investigate the adsorption potential of nitrate (NO_3^-), fluoride (F^-), phosphate (PO_4^{3-}), and sulphate (SO_4^{2-}) ions onto

cationic CNF. The effects of positive charge content and pH onto the adsorption capacity of the cationized CNF are investigated, as well as the selectivity against these contaminants. Finally, we exploit the functionality and network formation of cationic CNF for the preparation of permeable membranes intended for nitrate adsorption by filtration operations.

2. Materials and methods

2.1. Materials

Pulp residue, a waste product from pulp and paper industry also called “fiber sludge” (Jonoobi, Mathew, & Oksman, 2012), with a cellulose and hemicellulose content of 95% and 4.75%, respectively, was kindly provided by Processum AB, Sweden. Sodium hydroxide (NaOH) and glycidyltrimethylammonium chloride were purchased from Sigma–Aldrich.

2.2. Synthesis of cationic CNF

Cationic CNF preparation was reported elsewhere (Sehaqui, Perez de Larraya, et al., 2015) and adapted from a previous work (Pei et al., 2013). Pulp fibers were mechanically beaten and then mixed overnight with an aqueous solution of NaOH to obtain a suspension with final concentrations of 5 wt% and 2.5 wt% for NaOH and the pulp fibers, respectively. Three different amounts of glycidyltrimethylammonium chloride (Aldrich) were added to the suspension and the reaction was carried out at 65 °C for 8 hours under stirring. These three quantities of reactant correspond to molar ratios between hydroxyl groups of cellulose and ammonium functions of 1:1, 1:3 and 1:10. The reaction mixture was then neutralized with hydrochloric acid, filtered and washed thoroughly with deionized water. This chemically treated pulp was dispersed in water at a concentration of ~0.3 wt%, mixed for 10 min in an inline-dispersing system equipped with an Ultra-Turrax (IKA T25), and disintegrated using a high-shear homogenizer (M-110EH, Microfluidics Ind., Newton, MA) with two interaction chamber combinations and pressures up to 1200 bar. Cationic cellulose nanofibers obtained are denoted CNF-N, with N referring to the increase in the positive charges content. Non-modified nanofibers disintegrated from the waste pulp are taken as reference and are denoted CNF-0.

2.3. Physico-chemical characterisations

Few drops of CNF suspension at 0.1 wt% were placed on a specimen holder, sputter-coated directly with a platinum layer of about 7.5 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Liechtenstein) in Ar as a carrier gas at 0.05 mbar and SEM was carried out using a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA) at an accelerating voltage of 5 kV and a working distance of 5 mm. The molar quantity of trimethylammonium chloride groups on the quaternized CNF was estimated by conductometric titration of chloride ions with silver nitrate (Hasani et al., 2008). ζ -Potential measurements were performed on unmodified and quaternary modified CNF suspensions at ~0.1 wt% concentration using a Zetasizer NanoZS instrument (Malvern, UK). Thermal degradation of the CNF was studied by means of thermogravimetric analysis (TGA). Experiments were performed in a TGA7 instrument by Perkin Elmer under helium flow (25 ml min⁻¹) from 30 °C to 800 °C at a rate of 20 K min⁻¹ with maintaining the temperature at 100 °C for 15 min. Light transmittance of nanofiber suspensions was measured using a UV-Visible spectrophotometer (Shimadzu UV-3600) by placing the suspension

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