



## Research paper

# Efficient continuous removal of nitrates from water with cationic cellulose nanopaper membranes

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## Abstract

Nitrates constitute a severe problem for the quality of potable water. The removal of nitrates from water can be performed utilizing continuously operating cellulose nanopaper ion-exchangers, which so far are unfortunately of only moderate efficiency. Here we demonstrate cationic cellulose nanopapers comprising cellulose nanofibrils carrying a high amount of ammonium groups ( $1.6 \text{ g mmol}^{-1}$ , i.e.  $0.62 \text{ mmol g}^{-1}$ ), which are anticipated to enable efficient removal of nitrate ions from aqueous solutions. Thin nanopapers were shown to have high adsorption capacities. Therefore we prepared low grammage nanopapers using a papermaking process from cellulose nanofibrils prepared from paper mill sludge. The performance of these cationic nanopapers was characterized by their permeance, with these new cationic nanopapers having a permeance of more than  $100 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ , which is far greater than the permeance of conventional nanopapers. Furthermore, nitrate ions were successfully removed from water by capturing them through adsorption onto the cationic nanopaper by primarily an ion-exchange mechanism. These cationic nanopapers possessed adsorption capacities of almost  $300 \text{ mg g}^{-1}$ , which is superior to commonly used nanopaper ion-exchangers and batch-wise applied adsorbents. Utilization of an industrial side-stream in combination with very good membrane performance demonstrates the use of resource efficient technologies in an important sector.

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**Keywords:** Nanocellulose; Adsorption; Nitrates; Membrane

## 1. Introduction

Potable water containing high concentrations of nitrate ions constitutes a severe hazard to human health [1,2]. Responsible for the accumulation of nitrates in water sources is their high water solubility, whereby they are easily leached into the main drinking water reservoirs, i.e. ground water wells or rivers [3]. The most important origin of nitrates is effluents from the agricultural industry due to manure run-off and fertilizers [4]. Furthermore,  $\text{NO}_x$  air stripping waste from air pollution control devices, landfill leachate, leakage from septic

systems or unsafe disposal of untreated sanitary and industrial wastes also contribute [5,6]. Above a certain threshold, concentrations around  $15 \text{ mg L}^{-1}$ , nitrates are considered to be harmful to humans [7]. Negative health effects caused by too high nitrate uptake include the formation of carcinogenic nitrosamines in the human body [8,9] and methemoglobinemia [10]. Therefore, legislation aims to limit the concentration of nitrates in potable water, e.g. in the United States [4] and the European Union (Nitrates Directive (91/676/EEC)): Following a recommendation by the WHO [11], the concentration of nitrate ions in drinking water must not exceed  $50 \text{ mg L}^{-1}$ . Even though this value exceeds already the potentially harmful concentration, due to water shortage and extensive use of fertilizers this limit is, however, often exceeded, in particular in arid and semi-arid areas having a hot and dry climate [6]. Clearly, research to develop new and improve existing methodologies for the treatment of water

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containing high concentrations of nitrate ions is of utmost importance.

There are many different processes and methodologies used for the removal of nitrates; Adsorption and membrane processes are among the most prominent ones [3,12–17]. Moreover, chemical [18] and microbiological denitrification [19,20], (photo)catalytic processes [21–24], membrane bioreactors [25], electroreduction and electrocoagulation [26] as well as electrodialysis [27] are often used for this purpose. Unfortunately, all of these processes have drawbacks, such as batch-wise operation when using adsorbent materials [5] and disposal issues of saturated adsorbents [3]. Membrane processes such as reverse osmosis and nanofiltration on the other hand can be operated continuously with the opportunity of back-wash procedures [2,28] but suffer from low permeability requiring high pressures of up to 50 bar and thus a lot of energy [29]. Also the membrane materials themselves impose problems, as both synthetic polymers [30] and ceramics [31] have high energy and resource requirements. Thus it would be of great interest to have a renewable adsorbent material at hand that can be easily processed into an adsorption membrane with high affinity towards nitrate ions, hence combining these two approaches.

One possible candidate potentially fulfilling these requirements is nanofibrillated cellulose (CNF) [32], which can be easily modified [33] and processed into nanopapers [34–37]. Nanopapers have already been used in various membrane applications, but the drawback of moderate permeance and affinity to contaminants so far reduced their applicability [38,39]. In order to remove nitrates by adsorption on CNF, functional, positively charged moieties, such as ammonium groups, have to be attached onto the surface of the cellulose nanofibrils [40]. Cationic CNFs, carrying quaternary ammonium groups, have already been used as ion-exchange nanopaper [41]. Unfortunately, the permeance and adsorption capacity of nitrate ions of these nanopapers was only moderate. These drawbacks could be circumvented by increasing the concentration of ammonium groups on the surface of the CNF and the use of thinner nanopapers. It was shown that the highest affinity towards charged contaminants was achieved when using thin nanopapers because the contribution of functional groups on the surface of the nanopapers to the overall adsorption capacity is considered higher compared to functional groups in the bulk of the nanopapers [39,41].

Here we study the effect of a high ammonium content of cationic CNF and nanopaper thickness on the permeance and adsorption capacity of nitrate ions on cationic nanocellulose nanopapers. CNFs were produced from ammoniated paper mill fibre sludge. The CNFs were characterized by means of IR and elemental analysis. Nanopapers prepared from these CNFs were characterized by SEM and measurement of their zeta-potential and tested for their permeance and nitrate adsorption capacity.

## 2. Experimental procedures

### 2.1. Materials

Fibre sludge with a cellulose and hemicellulose content of 95% and 4.75%, respectively, was kindly supplied by

Processum AB. HCl, KCl, NaOH, KOH, NaNO<sub>3</sub> and glycidyltrimethylammonium chloride (GTMAC) were purchased from Sigma-Aldrich. All chemicals were used without further purification. For all procedures deionized water was used.

### 2.2. Preparation of cationic CNF

Paper mill fibre sludge was modified aiming to introduce a high concentration of ammonium moieties following a procedure adopted from literature [40,42]. The modified sludge was mechanically beaten and mixed with a solution (3 wt.-%) of NaOH, resulting in a suspension (5 wt.-%) of cellulose fibrils. These fibrils were modified with an aqueous solution (90%) of GTMAC at 80 °C for 8 h under stirring. Subsequently, this suspension was neutralized with HCl (1 mol L<sup>-1</sup>) and filtered, followed by thorough washing with deionized water. This dispersion of modified sludge was mixed for 10 min using an Ultra-Turrax (IKA T25) and finally disintegrated in a microfluidizer (M-110EH, Microfluidics Ind.) at room temperature and a pressure of 1600 bar to produce a suspension of cationic CNF (CCNF). The chemical composition of CCNF was investigated by ATR-FT-IR spectroscopy and elemental analysis, carried out using a 2400 CHN Elemental Analyzer from Perkin Elmer. The nitrogen content as determined by elemental analysis was used to determine the amount of ammonium groups attached to the CCNF.

### 2.3. Manufacturing of cationic nanopapers

The protocol to produce CCNF nanopapers was adopted from previous studies [34,36]. Briefly, after adjusting the consistency of the CCNF dispersion to 0.3 wt.-%, it was blended (Braun Multiquick 5 MX 2050) for 2 min to produce a homogeneous suspension of CCNF in water. This suspension was subsequently vacuum-filtered onto a cellulose filter paper (VWR 413, 5–13 µm pore size) to facilitate the formation of a wet filter cake, which was then wet-pressed for 5 min between blotting papers (3MM Chr VWR) under a weight of 10 kg to remove excess water. Thereafter, the still wet filter cakes were sandwiched between fresh blotting papers and metal plates and consolidated in a hot-press (25-12-2H, Carver Inc.) under a compression weight of 1 t for 1 h at 120 °C. Nanopapers with grammages (the mass of the paper per unit area) of 5, 10, 20 and 30 g m<sup>-2</sup> (gsm) were prepared.

### 2.4. Characterization of cationic nanopapers

#### 2.4.1. Surface charge of nanopapers

The surface charge of the CCNF nanopapers was investigated by measuring the ζ-potential as a function of pH with a SurPASS electrokinetic analyzer (Anton Paar). The nanopapers were mounted in an adjustable gap cell at a gap width of 100 µm and a solution of 1 mmol L<sup>-1</sup> KCl, as electrolyte, was pumped through the cell while the pressure drop was steadily increased to 300 mbar. By titrating 0.05 mol L<sup>-1</sup> HCl and 0.05 mol L<sup>-1</sup> KOH into the electrolyte solution, the pH was adjusted.

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