TOMSK POLYTECHNIC UNIVERSITY

Available online at www.sciencedirect.com

ScienceDirect

Resource-Efficient Technologies 3 (2017) 22–28

www.elsevier.com/locate/reffit

Research paper

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

Andreas Mautner [a,b,*], Thawanrat Kobkeatthawin [a,c], Alexander Bismarck [a,b]

[a] *Institute of Materials Chemistry & Research, Polymer & Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, 1090 Vienna, Austria*

[b] *Polymer & Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, SW7 2AZ London, United Kingdom*

[c] *Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Songkhla 90110, Thailand*

Received 24 October 2016; received in revised form 20 December 2016; accepted 22 January 2017

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 ($1.6\ \mathrm{g\ mmol^{-1}}$, i.e. $0.62\ \mathrm{mmol\ g^{-1}}$), 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 $100\ \mathrm{L\ m^{-2}\ h^{-1}\ MPa^{-1}}$, 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 $300\ \mathrm{mg\ g^{-1}}$, 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.

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, 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 $15\ \mathrm{mg\ L^{-1}}$, 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 $50\ \mathrm{mg\ L^{-1}}$. 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

---

* Corresponding author. Institute of Materials Chemistry & Research, Polymer & Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währingerstr. 42, A-1090 Vienna, Austria. Fax: +43 (1) 4277 871302.

E-mail address: andreas.mautner@univie.ac.at (A. Mautner).

http://dx.doi.org/10.1016/j.reffit.2017.01.005

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, $NaNO_3$ 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^{-1}) 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^{-2} (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^{-1} KCl, as electrolyte, was pumped through the cell while the pressure drop was steadily increased to 300 mbar. By titrating 0.05 mol L^{-1} HCl and 0.05 mol L^{-1} KOH into the electrolyte solution, the pH was adjusted.

2.4.2. Morphology of nanopapers

The morphology of the nanopapers was studied using SEM using a Zeiss Supra 55 VP operated at an accelerating voltage of 2 kV and a working distance of 7.3 mm. Specimens cut from CCNF nanopapers were placed on a specimen holder and directly sputter-coated with a gold layer of about 4 nm.

2.4.3. Nanopaper membrane performance: permeance and nitrate adsorption

The membrane performance of CCNF nanopapers was investigated by measuring the nanopaper permeance and performing nitrate adsorption studies. Filtration experiments, to determine the nanopaper permeance, were carried out in a dead-end stirred cell (Sterlitech HP4750). Discs (49 mm in diameter) were cut from the nanopapers, placed on a porous stainless steel support and installed into the dead-end cell. Deionized water was forced through the nanopapers using a head pressure of 0.2 MPa. By measuring the permeate volume per unit area per unit time, the water permeance [L m^{-2} h^{-1} MPa^{-1}] for the active filtration area (1460 mm^2) could be calculated.

To determine the nitrate adsorption capacity of CCNF nanopapers, a 5 mmol L^{-1} aqueous solution of $NaNO_3$ (pH 5.8) was forced through them. The permeate fractions were collected and analyzed using ion-chromatography. The mass of nitrate ions adsorbed per unit nanopaper area was calculated from the volume of each permeate fraction [mL] and the measured nitrate concentration [mg mL^{-1}] by subtracting the measured from the original concentration. The mass of adsorbed nitrate ions [mg] was then related to the membrane area [m^2] and plotted against the permeate volume [mL]. Subsequently, the sum of the mass of rejected nitrate ions [mg] could be determined and hence the mass of adsorbed nitrate ions [mg] per total mass of CCNF [g], i.e. the adsorption capacity [mg g^{-1}]. Furthermore, the concentration of chloride ions, exchanged with nitrate ions, in the permeate fractions was analyzed in parallel.

3. Results and discussion

3.1. Preparation of cationic CNF and CCNF nanopapers

Cationic CNFs (CCNFs) were prepared by the reaction (Fig. 1) of fibre sludge with glycidyltrimethylammonium chloride (GTMAC) and subsequent fibrillation following a procedure published previously [41] but with the aim of producing CCNF with a higher ammonium content. The successful attachment of GTMAC to cellulose was verified by ATR FT-IR spectroscopy. The existence of a new peak at a wavelength of 1480 cm^{-1} evidenced the successful introduction of the three methyl groups of the quaternized ammonium functionality [40,42]. A nitrogen content of 0.84% was determined using elemental analysis, which corresponds to 0.62 mmol g^{-1} ammonium groups, which is equivalent to a degree of substitution of 0.11. Thus, the ammonium content of CCNF was more than 50% bigger than for a CCNF grade used in our previous study [41].

Cationic CNF nanopapers containing various total amounts of ammonium groups were prepared from CCNF following a nanopaper making protocol [35,43,44]. The amount of ammonium groups available was controlled by setting the grammage (the mass of the paper per unit area [g m^{-2}]) of the nanopapers. Nanopapers with 5, 10, 20 and 30 g m^{-2} (gsm) were prepared. We demonstrated already [39,41] that the majority of charged contaminants are adsorbed on the surface of the nanopapers, thus we tried in this study to increase the ratio of surface ammonium groups to ammonium groups present in the bulk of the nanopapers. This should not only result in increased adsorption capacities but also lead to enhanced permeance.

The morphology of CCNF nanopapers was studied by means of scanning electron microscopy (SEM). Exemplarily, SEM images of a nanopaper with 30 gsm are shown in Fig. 2.

A relatively smooth surface morphology can be seen at low magnification (500×, Fig. 2, left). No defects or pinholes can be detected. At higher magnification (10,000×, Fig. 2, right), a random, homogeneous cellulose nanofibril network consisting of CNFs with a diameter around 50 nm can be seen. This morphology is typical for nanopapers prepared from cellulose nanofibrils.

For adsorption processes, one of the most important parameters influencing the efficiency is the surface charge of the adsorbent. The surface charge is characterized by the ζ-potential, which provides information about the type of functional moieties present on the surface. The ζ-potential as a function of pH (Fig. 3) was analyzed for CCNF nanopapers and compared to unmodified nanopapers (data from Reference [41]).

Due to a small amount of carboxyl groups, usually uronic acid groups produced by oxidation reactions during pulping [45], being commonly present in CNF, unmodified CNFs have negative ζ-potential between pH 2 and 9, with an extrapolated isoelectric point (i.e.p.) around pH 2. The lower ζ-potential at

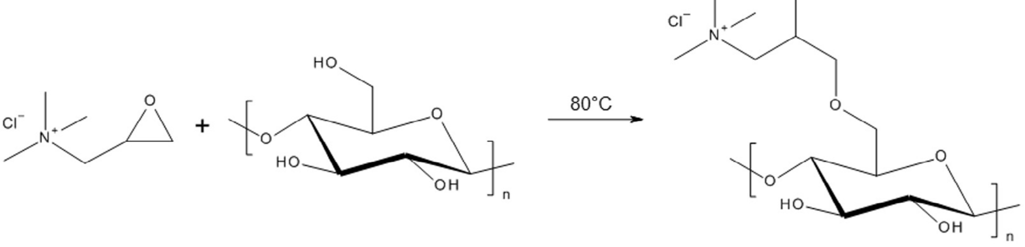

Fig. 1. Reaction of cellulose with GTMAC to attach quaternary ammonium groups.

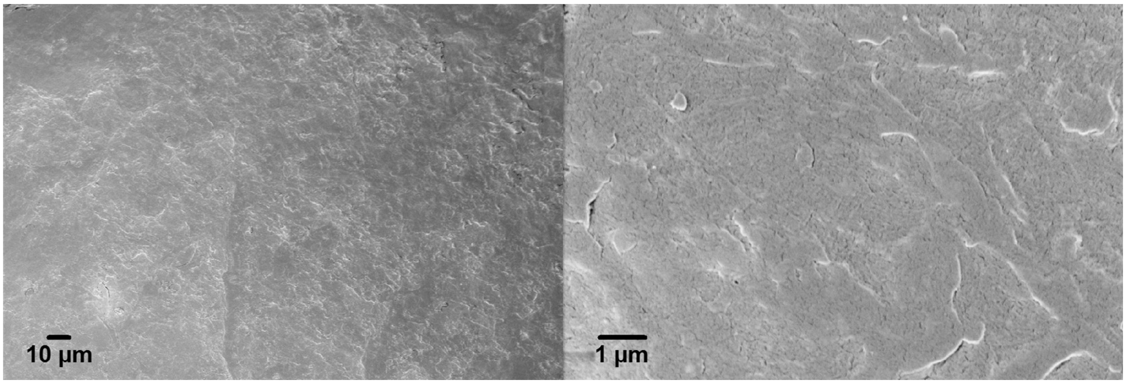

Fig. 2. SEM images of CCNF: magnification 500× (left) and 10,000× (right).

higher pH was attributed to the deprotonation of carboxyl groups. The ζ-potential levelled off on a plateau at around −28 mV, which indicates that all dissociable functional groups were fully deprotonated [35]. Cationically modified CNF nanopapers have a positive ζ-potential over the whole pH range analyzed, similar to values reported in other studies [45,46]. At pH 2, a ζ-potential of +36 mV was found, continuously decreasing with increasing pH to reach +9 mV at pH 9. This behaviour was explained by the protonation and deprotonation, respectively, of ammonium groups. At higher pH, protons were detached from the ammonium groups, resulting in uncharged amine-groups, which exhibited a ζ-potential close to zero. On the other hand, at low pH, due to the high concentration of protons in the environment, hardly any protons were detached from the ammonium groups, thus leaving them in their positively charged state, as indicated by a high, positive ζ-potential. The positive surface charge of CCNF nanopapers, as indicated by positive ζ-potential, is anticipated to enable efficient adsorption of nitrate ions.

3.2. Membrane performance of CCNF nanopapers

The performance of membranes is commonly evaluated by determination of the membrane permeance (*P*) and rejection of contaminants, in our case nitrate ions. The permeance of CCNF nanopapers was tested in a dead-end cell at 2 bar head pressure. Results of these measurements are shown in Fig. 4 and compared to unmodified CNF (data from Reference [36]).

Cationic nanopapers had a much higher permeance compared to unmodified nanopapers, reaching more than 100 L m^{-2} h^{-1} MPa^{-1}, which is a factor of three higher than the permeance of unmodified CNF nanopapers. The reason for this might be explained by different network densities. Due to the prevalence of charged groups, CCNF nanofibrils were readily repelled, thus giving rise to a lower network density and hence lower resistance to water passing the nanopaper. Both types of nanopapers, CCNF and unmodified CNF, exhibited an almost logarithmic relationship of permeance and grammage. This trend is typical for CNF nanopapers and was already found for various grades of CNF [34,36,39–41]. Most importantly, due to the low grammage and hence thickness, a very high permeance could be achieved. Cationic CNF nanopapers so far reached permeances up to 30 L m^{-2} h^{-1} MPa^{-1} [41]. The new CCNF nanopapers had a three times higher permeance. Since the overall performance of a membrane is very much dependent on the permeance, this corresponds to a three times better performance.

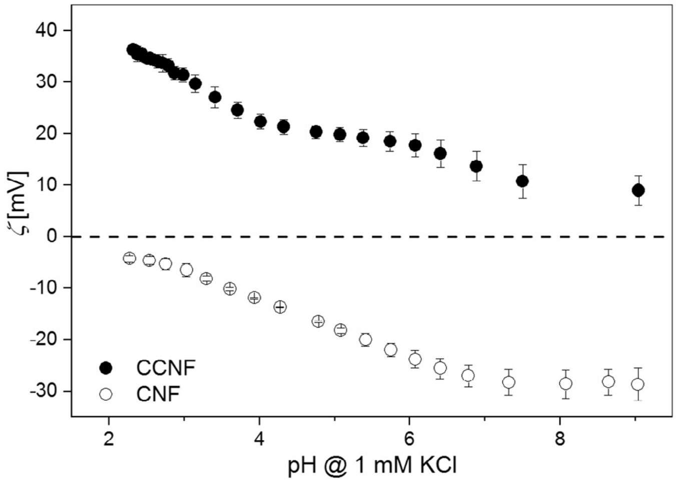

Fig. 3. ζ-Potential of CCNF nanopapers compared to unmodified CNF nanopapers (data from Reference [41]) as a function of pH.

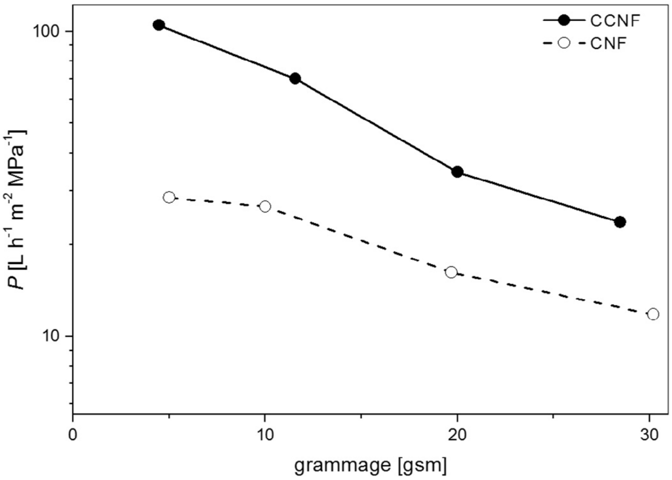

Fig. 4. Permeance of CCNF nanopapers as a function of grammage compared to unmodified CNF nanopapers (data from Reference [36]).

Adsorption of nitrate ions on cationic CNF has already been demonstrated in both static and dynamic adsorption experiments [40,41]. Unfortunately, particularly in dynamic filtration experiments, only moderate adsorption capacities were found. This was due to relatively thick membranes in which functional groups in the bulk of the nanopaper, compared to moieties present on the surface of the nanopapers, contributed only very little to the overall adsorption capacity. Moreover, the concentration of ammonium groups on the surface of the CNF was not optimized then. Hence it was the aim of this study, apart from increasing the amount of ammonium groups attached to the CNF, to prepare nanopapers as thin as possible to increase the permeance and adsorption capacities by increasing the fraction of ammonium groups present on the surface of the nanopapers. As shown before, this strategy was successful in the case of increased permeance. To evaluate the performance of these thin, high ammonium content CCNF nanopapers regarding adsorption capacity of nitrate ions, filtration experiments were performed.

Dynamic adsorption characteristics of CCNF nanopapers were analyzed using an aqueous solution of sodium nitrate (5 mmol L^{-1}). The concentration chosen was equivalent to 310 mg L^{-1}, thus being a nitrate loading, which corresponds to strongly nitrate contaminated water. The mass and amount of nitrate ions removed from the particular fraction were related to the active membrane area used and plotted as a function of the permeate volume, as exemplarily shown for 5 gsm and 30 gsm CCNF nanopapers (Fig. 5).

A continuous increase in nitrate ions adsorbed with increasing permeated volume was found until the nanopapers were completely saturated after around 50 mL of the test solution passed the nanopapers. The values at the saturation level were 2300 mg m^{-2}, 2150 mg m^{-2} and 1300 mg m^{-2}, for 30, 20 and 5 gsm nanopapers, respectively. This showed that the thicker and higher the grammage of the nanopapers is, the more nitrate ions could be adsorbed, which is what one would expect. However, there was no linear relationship between the amount of nitrate ions adsorbed and the nanopaper grammage. If the 30 gsm nanopapers were as effective as the 5 gsm nanopapers, a value of 7800 mg m^{-2} should have been found, which was not the case. The reason for this is that the adsorption efficiency of ammonium groups located on the surface of the nanopapers is higher compared to ammonium groups hidden in the bulk of the nanopapers. These were less available to nitrate adsorption due to spatial restrictions. Furthermore, interactions between uronic acid groups and ammonium groups could have led to inactivation of the ammonium groups, thus not being available for adsorption of nitrate ions anymore. However, even the thicker nanopapers were superior in terms of adsorption efficiency compared to cationic nanopapers in a previous study [41], which could adsorb only a moderate amount of nitrate ions per unit area of 380 mg m^{-2} and 390 mg m^{-2} for 30 gsm and 50 gsm, respectively. This was explained by the much higher number of ammonium groups attached to the CCNF nanofibrils and the utilization of thinner nanopapers.

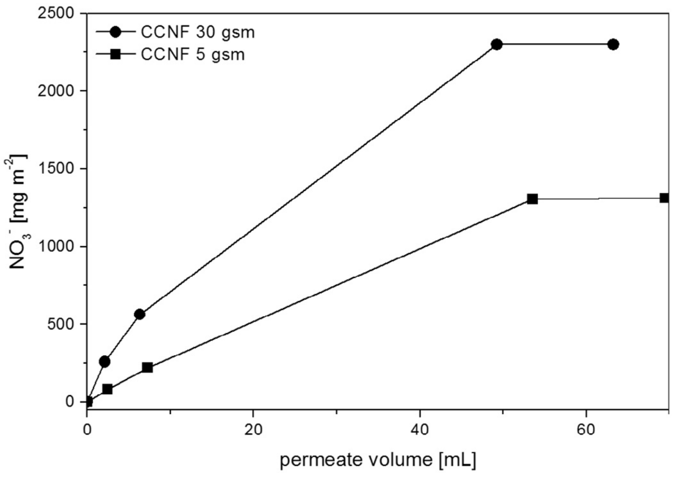

Fig. 5. Mass of adsorbed nitrate ions per unit filtration area vs. permeate volume for CCNF nanopapers with 5 gsm and 30 gsm, respectively.

Table 1
Adsorption capacities for CCNF nanopapers with different grammages.

Grammage [gsm]	Adsorption capacity	
	[mg g^{-1}]	[mmol g^{-1}]
5	293	4.7
20	113	1.8
30	81	1.3

From the value of the saturation level of the amount of adsorbed ions per unit area, the adsorption capacity was calculated for an active filtration area of 1460 mm^2 (Table 1).

For the thin 5 gsm CCNF nanopapers an adsorption capacity of almost 300 mg g^{-1} was found, which is outperforming many adsorbents used for nitrate removal [5]. For example, chitosan beads usually exhibit adsorption capacities around 100 mg g^{-1}. Adsorbents based on agricultural residues, e.g. straw charcoals, have even lower adsorption capacities of around 1 mg g^{-1}. In addition, it needs to be stressed that these adsorbents are typically tested in static environments with contact times of several hours, whereas the nanopaper membranes were tested in filtration operations.

In general, thicker nanopapers had considerably lower adsorption capacities, which was explained by a lower availability of ammonium groups in the bulk of nanopapers compared to ammonium groups on the surface of the nanopapers. Thus the conclusion can be drawn such that the fraction of functional groups on the surface of the nanopapers should be as high as possible in order to produce high adsorption capacities and thus efficient adsorbents. The efficient removal of nitrate ions from aqueous solutions can be related to the high positive ζ-potential. The positive surface charge was due to the attachment of ammonium groups onto the surface of the cellulose nanofibrils thus turning the usually negatively charged fibrils positive.

The mechanism of nitrate adsorption is anticipated to be based on ion-exchange of the counter-ions of the ammonium groups, chloride-ions, with nitrate ions. Furthermore, also electrostatic interaction between the functional groups attached to the cellulose nanofibrils and the nitrate ions is expected to play

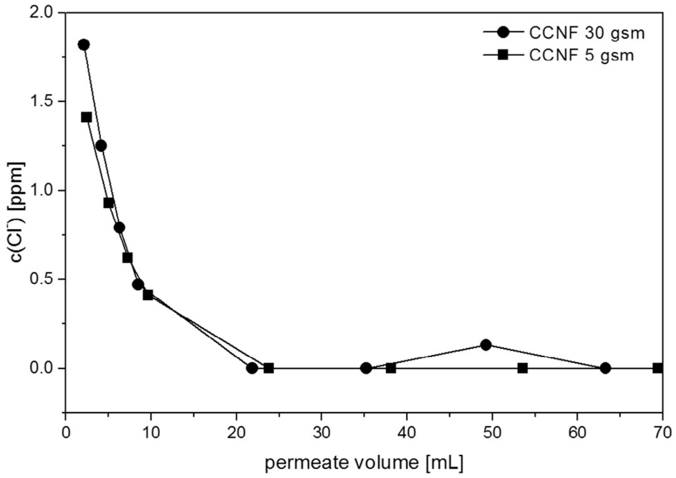

Fig. 6. Concentration of chloride ions exchanged with nitrate ions in the permeate fractions.

a significant role in the process. To study the mechanism of nitrate adsorption on ammonium modified CNF nanopapers, the concentration of chloride ions in the permeate was analyzed by ion-chromatography parallel to the nitrate concentration (Fig. 6).

Initially a high concentration of chloride ions was found in the permeate fractions. This showed that especially in the beginning of the filtration experiment, chloride ions were exchanged rapidly with nitrate ions. This observation indicated that the removal of nitrate ions by CCNF was initially based on an ion-exchange mechanism. However, already after 20 mL of the testing solution had permeated the nanopapers, hardly any chloride ions were found, but the adsorption of nitrate ions continued until a permeate volume of more than 50 mL was reached. Thus, it is not only the exchange of chloride ions with nitrate ions that is responsible for the removal of nitrate ions, but nitrates are also adsorbed on cationic CCNF nanopapers without ion-exchange taking place.

4. Conclusions

Cationic cellulose nanofibrils (CCNFs) containing a high amount of ammonium groups were prepared from ammoniated paper mill fibre sludge. ATR FT-IR spectroscopy and elemental analysis were used to prove the success of the modification. Nanopapers were prepared from CCNF utilizing a papermaking process. Nanopapers with various grammages were prepared with the focus on thin nanopapers, which were anticipated to show efficient adsorption of nitrate ions resulting in high adsorption capacities. The cationic nanopapers had a positive ζ-potential over the whole pH range tested. It was found that the performance of the nanopapers, as expressed by their permeance and adsorption capacity, was highly dependent on the thickness and thus the grammage of the nanopaper; thinner nanopapers had a higher permeance and adsorption capacity. Generally, cationic nanopapers made of CCNF had a higher permeance compared to common nanopapers prepared from unmodified CNF. This can be explained by the lower network density arising from the repulsive interaction between positively charged ammonium groups. Ultimately, it could be demonstrated that the CCNF nanopapers had a very high affinity towards nitrate ions, even under dynamic conditions during filtration experiments. Nitrate ions could be adsorbed by CCNF nanopapers up to 2300 mg per m^2 filtration area, which corresponds to adsorption capacities of more than 290 mg nitrate per g active adsorption agent. Furthermore, it was observed that the thinner the nanopaper is, the higher the adsorption capacity, which confirmed the results of similar studies previously published. It could be shown that quaternary ammonium groups on the nanopaper surface are more accessible for nitrate adsorption than the ammonium moieties in the bulk of the nanopapers. This was explained by the better availability of functional groups on the surface of the nanopapers. Ammonium groups in the bulk of nanopapers on the other hand were less available due to spatial restrictions and possible interactions of ammonium functionalities with uronic acid groups. Moreover, it was demonstrated that the mechanism of nitrate removal was primarily based on ion-exchange of chloride ions with nitrate ions, whereby even after all available chloride ions were exchanged adsorption still continued. It was concluded that the concentration of ammonium groups on CNF, in particular on the surface of nanopapers, is the most important parameter for efficient removal of nitrate ions in continuous filtration processes. Ultimately, it was shown that starting from an industrial side-stream it was possible to produce high performance nanopapers for membrane processes which could be used for water treatment.

Acknowledgements

The authors acknowledge the support by Stephan Puchegger and the Faculty Center for Nanostructure Research of the University of Vienna for providing access to electron microscopy and Dr. Houssine Sehaqui from Empa Duebendorf (CH) for providing the raw materials. Funding provided by the European Commission via the EU FP7 project NanoSelect (Grant No. 280519) is also greatly acknowledged. T.K. acknowledges the Thailand Research Fund through the Royal Golden Jubilee PhD Program (PHD/0137/2554) for financial support.

References

[1] E. Eroglu, V. Agarwal, M. Bradshaw, X. Chen, S.M. Smith, C.L. Raston, et al., Nitrate removal from liquid effluents using microalgae immobilized on chitosan nanofiber mats, Green Chem. 14 (2012) 2682–2685.
[2] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature (London, U. K.) 452 (2008) 301–310.
[3] A. Bhatnagar, E. Kumar, M. Sillanpää, Nitrate removal from water by nano-alumina: characterization and sorption studies, Chem. Eng. J. 163 (2010) 317–323.
[4] C. Della Rocca, V. Belgiorno, S. Meriç, Overview of in-situ applicable nitrate removal processes, Desalination 204 (2007) 46–62.
[5] A. Bhatnagar, M. Sillanpää, A review of emerging adsorbents for nitrate removal from water, Chem. Eng. J. 168 (2011) 493–504.
[6] K. Riha, G. Michalski, E. Gallo, K. Lohse, P. Brooks, T. Meixner, High atmospheric nitrate inputs and nitrogen turnover in semi-arid urban catchments, Ecosystems 17 (2014) 1–17.
[7] P. Santamaria, Nitrate in vegetables: toxicity, content, intake and EC regulation, J. Sci. Food Agric. 86 (2006) 10–17.

[8] I.T. Vermeer, D.M. Pachen, J.W. Dallinga, J.C. Kleinjans, J.M. van Maanen, Volatile N-nitrosamine formation after intake of nitrate at the ADI level in combination with an amine-rich diet, Environ. Health Perspect. 106 (1998) 459–463.

[9] J.M. van Maanen, I.J. Welle, G. Hageman, J.W. Dallinga, P.L. Mertens, J.C. Kleinjans, Nitrate contamination of drinking water: relationship with HPRT variant frequency in lymphocyte DNA and urinary excretion of N-nitrosamines, Environ. Health Perspect. 104 (1996) 522–528.

[10] H.H. Comly, Cyanosis in infants caused by nitrates in well water, J. Am. Med. Assoc. 257 (1987) 2788–2792.

[11] WHO, Guidelines for Drinking-Water Quality, 4th ed., 2011.

[12] H. Demiral, G. Gündüzoğlu, Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse, Bioresour. Technol. 101 (2010) 1675–1680.

[13] S. Ebrahimi, D.J. Roberts, Sustainable nitrate-contaminated water treatment using multi cycle ion-exchange/bioregeneration of nitrate selective resin, J. Hazard. Mater. 262 (2013) 539–544.

[14] S. Chatterjee, D.S. Lee, M.W. Lee, S.H. Woo, Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate, J. Hazard. Mater. 166 (2009) 508–513.

[15] S. Chatterjee, S.H. Woo, The removal of nitrate from aqueous solutions by chitosan hydrogel beads, J. Hazard. Mater. 164 (2009) 1012–1018.

[16] J.J. Schoeman, Nitrate-nitrogen removal with small-scale reverse osmosis, electrodialysis and ion-exchange units in rural areas, Water SA 35 (2009) 721–728.

[17] A.H. Mahvi, M. Malakootian, A. Fatehizadeh, M.H. Ehrampoush, Nitrate removal from aqueous solutions by nanofiltration, Desalin. Water Treat. 29 (2011) 326–330.

[18] O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira, Nitrate reduction with hydrogen in the presence of physical mixtures with mono and bimetallic catalysts and ions in solution, Appl. Catal. B 102 (2011) 424–432.

[19] A. Kapoor, T. Viraraghavan, Nitrate removal from drinking water – review, J. Environ. Eng. ASCE 123 (1997) 371–380.

[20] J.Y. Park, Y.J. Yoo, Biological nitrate removal in industrial wastewater treatment: which electron donor we can choose, Appl. Microbiol. Biotechnol. 82 (2009) 415–429.

[21] N. Barrabés, J. Sá, Catalytic nitrate removal from water, past, present and future perspectives, Appl. Catal. B 104 (2011) 1–5.

[22] C.L. Constantinou, C.N. Costa, A.M. Efstathiou, Catalytic removal of nitrates from waters, Catal. Today 151 (2010) 190–194.

[23] M. Shand, J.A. Anderson, Aqueous phase photocatalytic nitrate destruction using titania based materials: routes to enhanced performance and prospects for visible light activation, Catal. Sci. Technol. 3 (2013) 879–899.

[24] C.P. Theologides, P.G. Savva, C.N. Costa, Catalytic removal of nitrates from waters in a continuous flow process: the remarkable effect of liquid flow rate and gas feed composition, Appl. Catal. B 102 (2011) 54–61.

[25] E.J. McAdam, S.J. Judd, A review of membrane bioreactor potential for nitrate removal from drinking water, Desalination 196 (2006) 135–148.

[26] A.S. Koparal, Ü.B. Öğütveren, Removal of nitrate from water by electroreduction and electrocoagulation, J. Hazard. Mater. 89 (2002) 83–94.

[27] L.J. Banasiak, A.I. Schäfer, Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter, J. Membr. Sci. 334 (2009) 101–109.

[28] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, J. Membr. Sci. 83 (1993) 81–150.

[29] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712–717.

[30] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination. Development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.

[31] K. Li, Ceramic Membranes for Separation and Reaction, John Wiley & Sons, Ltd., Chichester, UK, 2007.

[32] D. Klemm, F. Kramer, S. Moritz, T. Lindstroem, M. Ankerfors, D. Gray, et al., Nanocelluloses: a new family of nature-based materials, Angew. Chem. Int. Ed. Engl. 50 (2011) 5438–5466.

[33] Y. Habibi, Key advances in the chemical modification of nanocelluloses, Chem. Soc. Rev. 43 (2014) 1519–1542.

[34] A. Mautner, K.Y. Lee, P. Lahtinen, M. Hakalahti, T. Tammelin, K. Li, et al., Nanopapers for organic solvent nanofiltration, Chem. Commun. 50 (2014) 5778–5781.

[35] K.-Y. Lee, T. Tammelin, K. Schulfter, H. Kiiskinen, J. Samela, A. Bismarck, High performance cellulose nanocomposites: comparing the reinforcing ability of bacterial cellulose and nanofibrillated cellulose, ACS Appl. Mater. Interfaces 4 (2012) 4078–4086.

[36] A. Mautner, K.-Y. Lee, T. Tammelin, A.P. Mathew, A.J. Nedoma, K. Li, et al., Cellulose nanopapers as tight aqueous ultra-filtration membranes, React. Funct. Polym. 86 (2015) 209–214.

[37] M. Hakalahti, A. Mautner, L.-S. Johansson, T. Hänninen, H. Setälä, E. Kontturi, et al., Direct interfacial modification of nanocellulose films for thermoresponsive membrane templates, ACS Appl. Mater. Interfaces 8 (2016) 2923–2927.

[38] G. Metreveli, L. Wågberg, E. Emmoth, S. Belák, M. Strømme, A. Mihranyan, A size-exclusion nanocellulose filter paper for virus removal, Adv. Healthc. Mater. 3 (2014) 1546–1550.

[39] A. Mautner, H.A. Maples, T. Kobkeatthawin, V. Kokol, Z. Karim, K. Li, et al., Phosphorylated nanocellulose papers for copper adsorption from aqueous solutions, Int. J. Environ. Sci. Technol. 13 (2016) 1861–1872.

[40] H. Sehaqui, A. Mautner, U. Perez de Larraya, N. Pfenninger, P. Tingaut, T. Zimmermann, Cationic cellulose nanofibers from waste pulp residues and their nitrate, fluoride, sulphate and phosphate adsorption properties, Carbohydr. Polym. 135 (2016) 334–340.

[41] A. Mautner, H.A. Maples, H. Sehaqui, T. Zimmermann, U. Perez de Larraya, A.P. Mathew, et al., Nitrate removal from water using a nanopaper ion-exchanger, Environ. Sci. Water. Res. 2 (2016) 117–124.

[42] A. Pei, N. Butchosa, L.A. Berglund, Q. Zhou, Surface quaternized cellulose nanofibrils with high water absorbency and adsorption capacity for anionic dyes, Soft Matter 9 (2013) 2047–2055.

[43] M. Henriksson, L.A. Berglund, P. Isaksson, T. Lindström, T. Nishino, Cellulose nanopaper structures of high toughness, Biomacromolecules 9 (2008) 1579–1585.

[44] H. Sehaqui, A. Liu, Q. Zhou, L.A. Berglund, Fast preparation procedure for large, flat cellulose and cellulose/inorganic nanopaper structures, Biomacromolecules 11 (2010) 2195–2198.

[45] A. Olszewska, P. Eronen, L.-S. Johansson, J.-M. Malho, M. Ankerfors, T. Lindström, et al., The behaviour of cationic nanofibrillar cellulose in aqueous media, Cellulose 18 (2011) 1213–1226.

[46] M. Hasani, E.D. Cranston, G. Westman, D.G. Gray, Cationic surface functionalization of cellulose nanocrystals, Soft Matter 4 (2008) 2238–2244.