

Anionic nanofibrillated cellulose - a sustainable agent to recover highly soluble salts from industrial effluents

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Abstract

Utilisation of sodium (Na^+) containing alkali in the neutralisation of acidic industrial process waters rich in sulphate (SO_4^{2-}) produces effluents high in sodium sulphate (Na_2SO_4) reluctant to precipitate. Discharge of the saline effluents leads to permanent chemical stratification of the recipient freshwater systems, which prevents their annual overturn and the subsequent oxygen supply to hypolimnion. Novel and sustainable technologies are desperately needed to prevent the hazardous environmental impacts of saline effluents. We investigated the ability of anionic nanofibrillated cellulose (NFC) gels of three different consistencies to recover solubilised Na^+ and SO_4^{2-} from authentic circumneutral mining water onto a solid phase. The water was treated with the NFC gels in three sequential batches at three sorbent-to-solution ratios. NFC-induced changes in the ion concentrations were determined to calculate the Na^+ and SO_4^{2-} retention capacity and purification efficiency of the NFC gels.

All NFC gels efficiently and coincidentally removed Na^+ and SO_4^{2-} from the mining water. We concluded that Na^+ ions electrostatically adsorbed onto the deprotonated carboxyl groups of the anionic NFC and attracted SO_4^{2-} ions which also acted as bridging anions between the neighbouring nanofibrils. Decrease in the consistency of the NFC gel enhanced accessibility of the sorption sites and, consequently, promoted the ion retention. A high sorbent-to-solution ratio favoured the intermolecular interactions within the NFC gels, thus decreasing the number of available sorption sites. A high ionic strength of the effluent favoured the ion retention, indicating that anionic NFC is particularly suitable for the treatment of highly saline solutions. The best purification result was obtained at a moderate sorbent-to-solution ratio with a dilute NFC gel. This lowers the demand for the cellulose raw material and the treatment expenses. We conclude that anionic NFC, made of renewable materials, may serve as an efficient and sustainable purification agent for removal and recycling of highly soluble Na^+ and SO_4^{2-} from industrial effluents.

Keywords

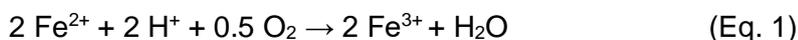
Nanofibrillated cellulose; Water treatment; Sorption; Ionic strength; Mining effluent

Abbreviations

FGD, Flue gas desulphurization; CN, Cellulose nanomaterial; NFC; Nanofibrillated cellulose; DM, Dry matter; EC, Electrical conductivity; *I*, Ionic strength; RO, Reverse osmosis

1. Introduction

Industries utilising sulphur- (S) containing raw materials or fuels, *e.g.* mining as well as power, pulp and paper industries, produce acidic process waters high in sulphate anions ($\text{HSO}_4^-/\text{SO}_4^{2-}$). In the mining industry, the acidity of the effluents originates from the extraction of economically valuable metals from sulphide ore minerals (*e.g.* chalcopyrite, CuFeS_2) typically co-occurring with pyrite (FeS_2) or iron sulphide (FeS) (Johnson, 2014). Bioleaching of metals by Fe- and S-oxidising bacteria generates sulphuric acid (H_2SO_4) according to Eqs. 1 and 2 (*e.g.* Johnson and Hallberg, 2005).



In pulp mills and power plants, combustion of S bearing materials, *e.g.* coal, heavy fuel oil, wood or peat, produces flue gases containing sulphur dioxide (SO_2), part of which further oxidise to sulphur trioxide (SO_3) (Srivastava *et al.*, 2004, Córdoba, 2015). Dissolution of SO_2 and SO_3 (referred to as SO_x) in water produces sulphurous (H_2SO_3) and sulphuric acid (H_2SO_4) according to Eqs. 3 and 4:



To avoid detrimental impacts of SO_x , various flue gas desulphurisation (FGD) techniques are applied. In the FGD processes, SO_x -containing gases, or their aqueous solutions, are subjected to scrubbing with industrial minerals, typically calcium carbonate (CaCO_3), hydroxide ($\text{Ca}(\text{OH})_2$) or

oxide (CaO), or alkaline chemicals e.g. sodium hydroxide (NaOH) or carbonate (Na₂CO₃) (Córdoba, 2015). The mining industry utilises the same neutralisation agents to reduce process water acidity and to precipitate residual solubilised metals as oxides and hydroxides (Coulton *et al.*, 2003, Johnson and Hallberg, 2005).

Neutralisation of H₂SO₄ with Ca-containing compounds generates sparingly soluble gypsum (CaSO₄·2H₂O) and, thus, somewhat reduces the SO₄²⁻ concentration of the effluent. Process water treatment with Na-containing alkali, in turn, produces highly soluble sodium sulphate (Na₂SO₄). Contrary to heavy metals, Na (pK_a 14.2, Lindsay, 1979, p. 121) does not precipitate even at a very high pH. Thus, Na⁺ and SO₄²⁻ ions remain soluble in the treated solution. If released into natural freshwater systems, the saline effluents of high density sink down to the hypolimnion and cause permanent chemical stratification of the water mass. This hinders its seasonal throughout circulations and, subsequently, prevents the supplementation of atmospheric oxygen in the hypolimnion. The resulting hypoxic or anoxic conditions in the sediment eventually lead to the release of Fe-bound phosphorus (P) from sediment to the ambient water and causes internal P loading and accelerates eutrophication of the water ecosystem (Patrick and Khalid, 1974, Smolders and Roelofs, 1993). Moreover, in freshwaters innately low in Na⁺ and SO₄²⁻, the highly saline effluents damage aquatic biota not naturally adapted to the osmotic stress (e.g. James *et al.*, 2003). In high concentrations, SO₄²⁻ is also toxic to certain freshwater invertebrates (Soucek and Kennedy, 2005). A high Na⁺ concentration, in turn, promotes the dispersion of sediment particles. The consequent turbidity hinders the light penetration and photosynthesis, causes injury to gill structures and suffocates organisms (Bilotta and Brazier, 2008).

To avoid detrimental impacts of salinisation of water systems, industrial effluents high in Na₂SO₄ require desalinisation before being discharged. Reverse osmosis (RO) is a common technique to treat saline effluents. In the pressure-driven process, solution is forced through a semi-permeable membrane that separates the solvent (water) from the electrolyte-rich phase of the solution. The purified filtrate (permeate) can be recycled or discharged, while the salt-concentrated phase of the solution (retentate) often requires treatment before being released to the environment (Van der

Bruggen *et al.*, 2003). Technologies such as various membrane-based and thermal treatments have been employed to decrease Na^+ and SO_4^{2-} concentrations of RO retentates (Perés-Gonzalés *et al.*, 2012). Adsorption or precipitation of solutes (e.g. CaSO_4) on the membrane surface, however, limits their applicability (Van der Bruggen *et al.*, 2003). Moreover, many of the techniques (including RO itself) are energy-intensive and have high operating costs (Van der Bruggen *et al.*, 2003, Perés-Gonzalés *et al.*, 2012). Thus, more convenient technologies to treat Na_2SO_4 -rich industrial effluents are desperately needed.

Biodegradable and environmentally inert nano- or microscale derivatives of cellulose (*i.e.* cellulose nanomaterials, CNs) manufactured from renewable natural materials may provide a novel and environmentally and economically sound option to treat Na^+ - and SO_4^{2-} -rich saline effluents. CNs rich in organic functional groups (hydroxyl (-OH), carboxyl (-COOH) and aldehyde (-COH)) can be chemically modified to render them anionic or cationic and thereby able to attract positively or negatively charged contaminants (Carpenter *et al.*, 2015).

There are a number of studies on the retention of heavy metal cations by anionic CNs from dilute solutions of pure chemicals (e.g. Saito and Isogai, 2005, Hokkanen *et al.*, 2013, Yu *et al.*, 2013, Kardam *et al.*, 2014, Sehaqui *et al.*, 2014, Suopajärvi *et al.*, 2015). Recently, Sehaqui *et al.* (2016) investigated the ability of a cationic CN to retain anions, including SO_4^{2-} . However, to our knowledge the retention of Na^+ and SO_4^{2-} by anionic CNs has been reported only in our previous paper (Venäläinen and Hartikainen, 2017). In the study carried out with highly acidic (pH 3.2) multimetal mining water we investigated the retention of metals and sulphate ions by anionic nanofibrillated cellulose (NFC) gel.

In the present study, a systematic adsorption experiment was carried out with anionic NFC (a) to investigate its capacity to retain Na^+ and SO_4^{2-} from an authentic neutralised mining water, and (b) to assess its utilisation as a purification agent in the treatment of saline effluents. Because NFC has a strong tendency to swell in water (Missoum *et al.*, 2013, Liu *et al.*, 2016), we hypothesised that the strength of mutual interactions between individual nanofibrils and, thus, the number of obtainable sorption sites, depend on the consistency of the NFC gel. Therefore, we investigated the sorption of

Na⁺ and SO₄²⁻ ions using anionic NFC gels of three different consistencies. Furthermore, to assess the efficiency of the gels to remove Na⁺ and SO₄²⁻ ions, we treated the authentic mining water with the NFC gels at three sorbent-to-solution ratios. All the treatments were carried out in three sequential batches to investigate whether a stepwise treatment with NFC promotes the removal of Na⁺ and SO₄²⁻ ions from the mining water and to unravel how a decrease in the ion concentration of the water affects the ability of NFCs to retain ions.

2. Materials and methods

2.1 Mining water

We received the mining water from Terrafame Ltd. (previously known as Talvivaara Mining Company Plc) located in Sotkamo, Finland (63°58'30"N 28°00'30"E), where nickel (Ni), zinc (Zn) cobalt (Co) and copper (Cu) are extracted from polymetallic sulphide ores through bioheapleaching. After recovery of the economically valuable metals from the pregnant leaching solution, part of the remaining effluent (raffinate) is returned to the bioheapleaching process. The rest of the raffinate undergoes stepwise neutralisation with CaCO₃ and Ca(OH)₂ to precipitate bulk Fe and other residual solubilised metals as oxides and hydroxides at pH ~10 (Terrafame, 2017). We carried out these experiments with the clarified water separated from the sludge in the sedimentation of metal precipitates. The process water was taken to mimic saline industrial effluents. It is noteworthy, however, that in the Terrafame mine these process waters undergo further treatment and pH adjustment before being discharged.

Preliminary pH measurement of the mining water revealed that its pH (6.5) was notably below 10. To determine the reason for the unexpected pH decrease, we took a water sample from a fresh, unopened container and subjected it to a continuous pH measurement (Mettler Toledo T70 titrator) for three days under stirring. Upon a 16-h exposure to atmospheric oxygen, the initial pH (9.6) of the mining water dropped to 7.6 and remained unchanged for the rest of the measurement. Due to the rapid decrease in the pH of the mining water upon its aeration, we decided to carry out our experiments on the oxidised solution with a circumneutral pH of 6.5 (measured with a pH meter

Consort C6010) to avoid changing pH conditions during the experiments. The solution was high in dissolved ions, as indicated by electrical conductivity (EC) of 7 mS cm^{-1} (measured with Mettler Toledo T70 titrator). The concentrations of Na^+ and SO_4^{2-} in the solution were 93 and 43 mmol L^{-1} (analysis method described in Section 2.3.2).

2.2 Nanofibrillated cellulose (NFC)

The NFC was provided by UPM Kymmene Oyj as a gel with a consistency of 2.8% (w/w). Anionisation and fibrillation of the material had previously been done by TEMPO-mediated oxidation in which the primary alcohols of cellulose are converted to aldehydes and carboxylic acids using NaClO as a primary oxidant (Saito *et al.*, 2007). The process is followed by mechanical dispersion of the anionic pulp to form a viscous gel. The charge density of the anionic pulp (determined by the manufacturer as the number of COOH -groups according to the Conductometric titration method SCAN-CM 65:02 (Scandinavian Pulp, Paper and Board Testing Committee, 2002)) was $1 \text{ mmol COOH g}^{-1}$ (dry matter, DM). We further diluted the NFC gel with Milli-Q[®] water to obtain dispersions having consistencies of 1.8% (NFC1.8), 1.4% (NFC1.4) and 1.1% (NFC1.1) (w/w) determined as weight loss after drying the dispersions ($60 \text{ }^\circ\text{C}$, 19 h). Each dispersion was investigated as a separate sorbent material. To ascertain a thorough incorporation of the added water into the hydration spheres of the NFC fibrils, we centrifuged the diluted samples (3600 rpm, 10 min, Hermle Labortechnik Z 513 K). No loose water separated out of the dispersions in centrifugation.

2.3 Experimental design

2.3.1 Experimental set-up

We performed stepwise adsorption tests with the anionic NFC gels (NFC1.8, NFC1.4 and NFC1.1) to investigate their capacity to retain Na^+ and SO_4^{2-} ions and to reduce their concentrations in the neutralised mining water. The experiments were carried out in three sequential batches (B1, B2 and B3) according to the following protocol:

- 1) In the first batch, the mining water was treated with a set of NFC gels at three different sorbent-to-solution ratios: 1:5, 2:5 or 3:5 V/V. After addition of the NFCs to the solutions, the

suspensions were carefully turned over twice to avoid breakdown of the NFC floccs formed in the reaction between the NFC gel and the solution. The suspensions were allowed to react for 10 min before passing through filter paper (Whatman® type 589/3) into plastic bottles (B1).

- 2) Next, the NFC-treated mining water samples obtained from the first batch were collected and aliquots of each filtrated solution were re-treated with fresh portions of NFC gels at the same sorbent-to-solution ratios as previously. After a 10-min reaction and subsequent filtration, the NFC-treated water samples were collected (B2).
- 3) Finally, aliquots of each solution obtained from the second batch were treated with a third set of fresh NFC gels as previously (B3).

Mining water controls, not treated with the NFCs, were prepared according to the same protocol. To rule out the retention of Na and S by the filter paper, the untreated mining water was analysed for Na and S before and after the filtration. All the treatments were carried out with three replicates. A schematic description of the experimental set-up is given in Fig. 1.

2.3.2 Chemical analyses of the mining water samples

The Na and S concentrations in all filtrates, as well as in the initial mining water, were determined with ICP-OES (Thermo Scientific iCAP 6000) at wavelengths of 589.5 nm for Na and 182.0 nm for S. To control the correct operation of the device, we analysed external standards of known concentrations (prepared from AccuStandard® Accutrace Reference Standard and Perkin Elmer® Pure Instrument Calibration Standard) every 20 samples. Due to the relatively high pH (6.5) of the mining water, all the S in the solution was expected to occur in the fully deprotonated SO_4^{2-} form ($\text{pK}_{\text{a}2}$ of H_2SO_4 being 1.98) (Lindsay, 1979, p. 284). Finally, we measured pH of all the filtrates (pH meter Consort C6010).

In the first batch treatment (B1), the NFC-induced removal of Na^+ and SO_4^{2-} from the mining water was calculated by subtracting their concentrations (mmol L^{-1}) in the NFC-treated samples (C_{B1}) from those in the control sample (C_0). In the second batch treatment (B2), the removal of the elements

was calculated by subtracting their concentrations after B2 (C_{B2}) from C_{B1} . Analogously, in the third batch treatment (B3), the removal of Na^+ and SO_4^{2-} was calculated by subtracting their concentrations after B3 (C_{B3}) from C_{B2} . The total NFC-induced removal (%) of Na^+ and SO_4^{2-} from the mining water after all three batch treatments was calculated according to Eq. 5:

$$[1 - ((C_0 - C_{B3}) / C_0)] \times 100\% \quad (\text{Eq. 5})$$

The Na^+ and SO_4^{2-} sorption *capacity* of the NFC gels (mol kg^{-1} DM) was calculated based on their removal in the first batch treatment.

2.3.3 Statistical analyses

The NFC-induced removal of Na^+ and SO_4^{2-} from the mining water in each batch treatment (B1, B2 and B3) with NFC1.8, NFC1.4 or NFC1.1 at each sorbent-to-solution ratio (1:5, 2:5 or 3:5) was calculated as an average of the three replicate samples. A standard deviation (SD) was calculated for the removal of Na^+ and SO_4^{2-} in each batch treatment. Statistical differences in the final pHs and the total NFC-induced removal of Na^+ and SO_4^{2-} between the triplicated treatments with NFC1.8, NFC1.4 or NFC1.1 at each sorbent-to-solution ratio (1:5, 2:5 and 3:5) were tested by one-way analysis of variance using Tukey's test for paired comparisons. Statistical analyses were carried out with SPSS 24.0 for Windows. The statistical significance was determined as $p \leq 0.05$.

3. Results

The addition of NFC gels to the mining water samples resulted in the formation of colourless flocs in the suspensions. After the first batch treatment (B1) with NFC of the highest consistency (NFC1.8), the solution phase of the suspensions passed through the filter paper considerably faster than the solution in the suspensions of NFC1.4 or NFC1.1. However, after the second and the third batch treatments (B2 and B3), all the NFC-treated suspensions became more viscous, which impeded and slowed down the permeation of the solution through the filter paper.

All NFC-treatments reduced the Na^+ and SO_4^{2-} concentrations in the mining water (Fig. 2 and 3). The total relative removal (%) of SO_4^{2-} regularly exceeded that of Na^+ . Treating the mining water in

three sequential batches substantially improved the purification result. The removal of both ion species was the highest in the first batch and decreased in the subsequent ones. Consequently, regardless of the treatment combination, the ion removal by triplicated treatment with the NFCs was two-fold compared to that by a single treatment. Doubling of the sorbent-to-solution ratio from 1:5 to 2:5 enhanced the total removal of Na^+ and SO_4^{2-} by 36 – 49% whereas a further increase in the ratio from 2:5 to 3:5 enhanced it only by 13 – 17%. Overall, the total removal of Na^+ by the triplicated NFC-treatment amounted to 34 – 71% and that of SO_4^{2-} to 43 – 85%.

Consistency of the NFC gels did not affect the purification result. At a given sorbent-to-solution ratio, the total ion removals by NFC1.8, NFC1.4 and NFC1.1 were equal (Fig. 2 and 3). The sorption capacity of the NFC gels (mol kg^{-1} DM), in turn, substantially increased upon decreasing their DM content (Table 1). Consequently, a single treatment with NFC1.1 retained approximately 25 – 80% more Na^+ and SO_4^{2-} than the NFC gels of higher consistencies (NFC1.4 and NFC1.8). It is noteworthy that, regardless of the consistency, the sorption capacity of a given NFC gel diminished with an increasing sorbent-to-solution ratio used. Tripling the sorbent volume lowered the ion sorption efficiency by 32– 40% (Table 1).

Each subsequent batch treatment with the NFC gels gradually lowered the pH of the filtrates. Upon the triplicated treatment, the initial pH of the mining water (6.5) had dropped to 4.7 – 4.3 in the final filtrates (Table 1). Surprisingly, a similar drop in pH was also detected in the control sample *i.e.* in the mining water not subjected to reaction with the NFCs, but otherwise handled the same way as the NFC-treated samples.

Treatment	V/V	pH	Na ⁺ (B1)	SO ₄ ²⁻ (B1)
		B1-B3	mol kg ⁻¹ ± SD	
None (Control)		6.4 - 4.6 ^{ab}		
NFC1.8	1:5	5.6 - 4.4 ^{ab}	4.9 ± 0.22	3.2 ± 0.53
	2:5	5.4 - 4.6 ^{ab}	3.7 ± 0.18	2.2 ± 0.01
	3:5	5.6 - 4.7 ^b	3.2 ± 0.23	1.9 ± 0.03
NFC1.4	1:5	5.1 - 4.3 ^a	6.7 ± 0.74	4.3 ± 0.29
	2:5	4.8 - 4.5 ^{ab}	5.3 ± 0.62	3.0 ± 0.12
	3:5	n.m. - 4.6 ^{ab}	4.3 ± 0.08	2.5 ± 0.01
NFC1.1	1:5	5.3 - 4.3 ^a	8.5 ± 0.87	5.4 ± 0.07
	2:5	4.7 - 4.5 ^{ab}	6.9 ± 0.15	3.9 ± 0.03
	3:5	4.8 - 4.7 ^b	5.8 ± 0.07	3.3 ± 0.03

Table 1. Capacity of NFC gels of different consistencies (NFC1.8, NFC1.4 and NFC1.1) to retain Na⁺ and SO₄²⁻ ions calculated based on their removal in the first batch treatment (B1), and the decrease in the pH of the mining water upon three sequential batch treatments (B1-B3) with the NFCs at sorbent-to-solution ratios of 1:5, 2:5 and 3:5 (V/V). Different letters in the superscript indicate statistically significant differences ($p \leq 0.05$) in the final pH between the various treatment combinations. In NFC1.4 (3:5), pH of the filtrate after B1 was not measured (n.m.) due to shortage of the sample solution.

4. Discussion

4.1 Impact of oxidation on the pH of the mining water

The rapid drop in the pH of the initial mining water upon the 16-h exposure to atmospheric oxygen indicates the presence of redox-sensitive metal residuals in the solution. In the Terrafame mine, the raffinate produced in the recovery process of metals is typically high in solubilised manganese (Mn) and Fe. If the removal of these metals in the lime neutralisation process is incomplete, their traces in the process water are prone to be further oxidised. Oxidation of the residual Mn²⁺ to Mn^{3+/4+} or Fe²⁺ to Fe³⁺ produces acidity, which explains the rapid drop in pH in this study. The mining water

used in our purification experiments was already oxidised as indicated by its pH (6.5) being clearly below 10. The primary oxidation most likely took place when the solution was transferred from its original container to a smaller one. During the purification experiment, the solution was re-exposed to oxidation in the pipetting, incubation and filtration steps, which explains the further decrease in pH detected in all filtrates after the three sequential batch treatments.

4.2 Mechanism of Na⁺ and SO₄²⁻ sorption onto the NFC gels differing in their consistencies

Contrary to various polyvalent cations (e.g. Al³⁺ or Fe³⁺), Na⁺ has a high ionic potential (*i.e.* high ratio of ion radius to ion charge) rendering it highly soluble and able to be retained electrostatically onto negatively charged surfaces. The capacity of NFC1.8, NFC1.4 and NFC1.1 to retain Na⁺ was, however, 3.2 – 8.5-fold compared to the negative charge density in the anionic cellulose pulp. This finding suggests that the conductometric titration method applied to determine the number of COOH-groups in the undispersed cellulose pulp is inadequate for estimating the charge density of the dispersed material. We hypothesise that, in the undispersed cellulose pulp, the inter- and intramolecular interactions (e.g. hydrogen bonds) within the cellulose fibrils reduce the activity of COOH-groups. Consequently, a large number of COOH-groups remain inactive during the conductometric titration, leading to the underestimation of their actual amount. Dispersion of the anionic pulp in water (*i.e.* formation of the NFC gel) decreases the interactions within the material, leading to higher activity of the COOH-groups. This phenomenon explains why the retention of Na⁺ by the NFC gels highly exceeded the estimated number of COOH-groups in the sorbent.

When dispersed in water at circumneutral pH, the acidic functional groups on the cellulose nanofibrils become more or less dissociated rendering the material negatively charged. Due to the coulombic repulsion between the negative charges within the fibrils, the material stretches out and becomes susceptible to strong hydration. The higher the consistency of the NFC gel, the stronger the attraction between the NFC surface and the water molecules. Upon addition of the NFC gels into the highly saline mining water, the negatively charged sites attracted the Na⁺ cations in the water, consequently

reducing the intramolecular repulsion within the cellulose nanofibrils. The reduced repulsion then increased the rigidity of the material. This was observed as the formation of flocs in the NFC-mining water suspensions particularly after the first batch treatment. When the Na^+ ions diffused towards the hydrated cellulose nanofibrils, they removed water from the hydration spheres. Consequently, the Na^+ concentration in the free solution phase of the suspension decreased.

At a given sorbent-to-solution ratio, the purification result obtained with NFC gel of a consistency of 1.1% equalled that obtained with those of higher consistencies (1.4% or 1.8%). Consequently, the actual Na^+ retention capacity (mol kg^{-1} DM) of the sorbent gel improved upon decreasing its DM content from 1.8% to 1.4% and 1.1%. In the NFC1.1, the extensive hydration increased the activity of the COOH-groups and enhanced the inter- and intramolecular repulsion of the cellulose nanofibrils, thus facilitating the accessibility of the negatively charged sorption sites. Moreover, the water in the strongly hydrated NFC1.1 was more easily removed by the adsorbing cations than that in the NFCs of higher consistencies (NFC1.4 or NFC1.8). This gel property, at least partly, explains the superior retention of Na^+ by the NFC1.1 gel. Hence, we conclude that the Na^+ retention capacity of the NFC gels was more attributable to the accessibility and activity of the negatively charged sorption sites than to their actual amount in the sorbent.

Upon diffusion of the cations towards the negatively charged sorption sites, the NFC surfaces became concentrated with cations which attracted the SO_4^{2-} ions and thereby lowered their concentration in the free solution phase. Despite the negative charge of the NFC fibrils, the *relative* retention of SO_4^{2-} exceeded that of Na^+ in all NFC-treatments. This phenomenon suggests that the multivalent SO_4^{2-} ions are not only attracted by the positively charged Na^+ ions on single cellulose nanofibrils, but they also act as bridging anions between the Na^+ cations sorbed onto the adjacent fibrils. Furthermore, provided the mining water also contains traces of polyvalent cations, their retention onto the negatively charged sorption sites would outweigh the retention of Na^+ . Sorption of polyvalent cations would contribute to the formation of the positively charged layer around the cellulose nanofibrils and thereby promote the retention of SO_4^{2-} .

The decrease in the removal of Na^+ and SO_4^{2-} from the mining water upon its repeated treatment with the NFC gels indicates that the retention efficiency is highly attributable to the ionic strength (I) of the ambient solution. The high I of the initial mining water (as indicated by an EC of 7 mS cm^{-1}) compressed the hydration spheres of the NFC fibrils and ions in the mining water, thereby facilitating their interactions with each other. Upon repeated treatments of the mining water with the NFC gels, however, the concentrations of Na^+ and SO_4^{2-} in the solution diminished. The subsequent decrease in I together with the concomitant decrease in pH expanded the hydration spheres of the ions and NFC fibrils. This phenomenon was observed as increased viscosity of the NFC-mining water suspensions in the second and third batch treatments. The increased hydration spheres of the NFC fibrils and ions weakened the ion retention. In addition, it is possible that the increased acidity of the mining water upon its sequential batch treatment promoted the protonation of the sorption sites and, subsequently, decreased the co-retention of Na^+ and SO_4^{2-} ions.

Increasing the sorbent-to-solution ratio from 1:5 to 2:5 (*i.e.* the increased volume of NFC added to the mining water) substantially improved the purification result. Doubling of the sorbent volume did not, however, double the *relative* retention of Na^+ and SO_4^{2-} . Upon further increase of the ratio to 3:5, the retention improved only a little. We conclude that when the suspension gets too crowded with the sorbent, the inter- and intramolecular attractions between the functional surface groups of cellulose nanofibrils outweigh the attractions between the sorbent and ions in the mining water, thus diminishing their retention. The same phenomenon explains why the Na^+ and SO_4^{2-} retention *capacity* of the NFC gels diminished upon increasing of the sorbent-to-solution ratio.

5. Conclusions

Anionic NFC gels were able to retain highly soluble Na^+ and SO_4^{2-} ions from authentic circumneutral mining water efficiently and simultaneously. Despite the very high water content of the sorbent gels (over 98%), triplicated treatment with the NFC gels removed as much as 71% of Na^+ and 85% of SO_4^{2-} from the highly saline mining effluent. The retention of Na^+ was taken to occur through electrostatic attraction by the deprotonated negatively charged carboxylate groups on the cellulose nanofibrils. The SO_4^{2-} ions were attracted by the positively charged Na^+ accumulated on the cellulose

nanofibrils and acted as bridging anions between the Na^+ ions occupying adjacent cellulose nanofibrils. Dispersion of the anionic pulp in water increases the activity of its COOH-groups. Furthermore, diluting the NFC gel with water to obtain the maximum hydration degree of the cellulose nanofibrils stretches out the configuration of the sorbent. This facilitates the accessibility of the sorption sites and substantially increases their capacity to retain Na^+ and SO_4^{2-} ions. On the other hand, an excessive sorbent amount promotes the mutual interactions between the functional surface groups of NFC in the gel and, consequently, reduces their capacity to retain Na^+ and SO_4^{2-} .

We conclude that anionic NFC, made of renewable material, is a promising agent to recover highly soluble salts from industrial effluents. Retention of the ions improves upon decreasing consistency of the NFC gel and the best purification result is obtained at a moderate sorbent-to-solution ratio. This reduces the demand for the cellulose raw material and the treatment expenses. Moreover, a high ionic strength of the mining water promotes the retention of Na^+ and SO_4^{2-} . Hence, anionic NFC gel proved to be suitable for purification of highly saline industrial effluents and, thus, a potential agent to be used in the preliminary treatment of concentrated process waters rich in Na^+ and SO_4^{2-} reluctant to precipitate even at high pH. Trapping the solubilised ions from a solution phase onto a solid sorbent renders their management easier. Furthermore, flocculation of the anionic NFC gel upon reaction with a highly saline effluent facilitates recovery of the used sorbent e.g. through flotation. Due to the organic nature of the NFC gel the sorbed ions may be liberated e.g. through combustion of the used NFC gel. As a result, the recovered ions will remain in the dry ash and, thus, may be easily recycled elsewhere.

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Figure captions

Fig.1. Schematic description of the experimental set-up

Fig. 2. The removal of Na⁺ ions (mmol L⁻¹) from the mining water in each batch treatment (B1, B2 and B3) with NFC gels of different consistencies (NFC1.8, NFC1.4 and NFC1.1) at sorbent-to-solution ratios of 1:5, 2:5 and 3:5 (V/V). SD of the removal is designated by the error bars. The total removal (%) given below the figure stands for the removal of Na⁺ ions by the triplicated NFC-treatment. Different letters above the columns indicate statistically significant differences ($p \leq 0.05$) in the total removal of Na⁺.

Fig. 3. The removal of SO₄²⁻ ions (mmol L⁻¹) from the mining water in each batch treatment (B1, B2 and B3) with NFC gels of different consistencies (NFC1.8, NFC1.4 and NFC1.1) at sorbent-to-solution ratios of 1:5, 2:5 and 3:5 (V/V). SD of the removal is designated by the error bars. The total removal (%) given below the figure stands for the removal of SO₄²⁻ ions by the triplicated NFC-treatment. Different letters above the columns indicate statistically significant differences ($p \leq 0.05$) in the total removal of SO₄²⁻.