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Rejection of inorganic and organic nitrogen species by nanofiltration: Opportunities for nitrogen circular economy☆

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ABSTRACT

Nanofiltration was used to reject various forms of nitrogen in water. Inorganic nitrogen (IN) species, including ammonium (NH_4^+), nitrates (NO_3^-), and nitrites (NO_2^-), as well as organic nitrogen (ON) compounds, such as urea, and organic matter (OM) with ON content were considered. The rejection of the different nitrogen compounds by nanofiltration was largely governed by the interplay between size exclusion and charge exclusion mechanisms. The characteristics of nitrogen species, including hydrated radius and charge valency, as well as membrane surface characteristics such as pore diameter and surface charge, were the contributing parameters. Varying pH and ionic strength contributed to the permeation of the charged nitrogen species (NH_4^+, NO_3^-, NO_2^-). The difference in rejection observed when varying pH was attributed to the speciation of some nitrogen species (NH_4^+, NO_2^-) in addition to pH dependent changes in the surface charge of the membrane. Increasing the ionic strength resulted in charge screening on the membrane surface, reducing the charge exclusion and thus enhancing the solute permeability. This was not the case for neutral species such as urea. The presence of different OM types with different molecular sizes and anionic charges enhances the rejection of the charged nitrogen species, such as NH_4^+, NO_3^-. This is potentially due to an increase in the membrane surface charge due to OM adsorption. ON, found mainly in biopolymers, humic substances, and low molecular weight fractions of the different OM types, was rejected by NF. The results demonstrate the potential of nanofiltration for rejecting diverse nitrogen compounds, thus providing a suitable technology for recycling nitrogen in water treatment processes. The findings contribute valuable insights for nitrogen separation and advancing sustainable nutrient management in the circular economy.

1. Introduction

1.1. Nitrogen in the aqueous environment

Nitrogen (N_2) on the earth's surface is controlled by the nitrogen cycle (N-cycle), which balances inorganic and organic N-compounds in nature [1,2]. While N species are valuable nutrients for soil fertility and biodiversity [3], excessive inputs from the overuse of nitrogenous fertilizers, discharge of wastewater effluents, and nitrous oxide emissions imbalance the N-cycle [4,5], and provoke the deterioration of environmental systems, particularly aquatic biodiversity, and water quality [6]. As a result, several aquifers around the world are affected by high concentrations of inorganic nitrogen (IN) species, particularly nitrate (NO_3^-) [7–9].

Concentrations higher than the World Health Organization (WHO) guideline for drinking water (50 $mg.L^{-1}$ as NO_3^- or 10 $mg.L^{-1}$ as N-NO_3^- [10] have been reported in 9 regions in Europe (51–2753 $mg.L^{-1}$), 20 regions in Asia (59–220 $mg.L^{-1}$), one region in South America (51 $mg.L^{-1}$), and 30 regions in Africa (52–776 $mg.L^{-1}$) [11]. While nitrite (NO_2^-), ammonium (NH_4^+), and organic nitrogen (ON) contamination in groundwater is less discussed compared to NO_3^-, their presence has been reported in various regions with intensive livestock farming, fertilizer use, and wastewater inputs [12–14].

1.2. Hazardous characteristics of nitrogen

The species NO_3^- and NO_2^- are tasteless and odorless, while NH_4^+ when converted to ammonia (NH_3), which is a pH-dependent reaction,

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can cause an unpleasant smell in water. Toxicity studies revealed that NO_2^- is more toxic than other inorganic forms of N [15]. In the human body, ingested NO_3^- is first reduced to NO_2^- followed by a second reduction to nitric oxide with both compounds disrupting oxygen transport in the blood, particularly in infants, causing blue baby syndrome [16]. Other health issues include cancer, thyroid defects, and birth defects [17,18].

The WHO drinking water guidelines for N-NO_2^- is 0.9 mg.L^{-1} (or 3 mg.L^{-1}as NO_2^-), while a threshold taste concentration (not a health-based guideline) of 27 mg.L^{-1} for N-NH_4^+ (or 35 mg.L^{-1} as NH_4^+) [10]. While no health-based guidelines are proposed for NH_4^+ and ON, such as urea, these N compounds contribute to the formation of disinfection by-products (DBPs) [19,20], such as nitrosamines, nitromethanes, and acetonitriles that can be formed following chemical disinfection processes in water treatment plants [21].

1.3. Nitrogen bound in organic matter

Nitrogen functional groups, such as amine, amide, and heterocyclic-N, are present in organic matter (OM), such as in the case of humic acid derived from soil with 0.9 to 3 % as N by weight [22,23]. OM derived from aquatic algae has relatively high ON content, due to photosynthesis in algae that converts the IN into more complex ON [24]. This is commonly found in eutrophic surface water bodies with high nutrient inputs [25]. The presence of ON in OM could result from the IN species binding to OM, which depends on the phenolic and carbonyl carbon content and the molecular weight (MW) fraction of OM [26]. A study revealed that IN can adsorb onto humic substances through cation exchange processes [27]. Monitoring both IN and ON throughout treatment and distribution is therefore essential, and their removal is required to ensure drinking water quality standards.

1.4. Nitrogen recovery in a circular economy

Circular nitrogen economy refers to the recycling of nitrogen, which is a critical element for agriculture and ecosystems, from waste to seek a balance of nitrogen inputs and outputs sustainably [28]. Such an economic system seeks to minimize waste and replace the end-life (waste disposal) by reusing, recycling, and replenishing resources, such as nutrients and water [29]. For example, reusing the nutrients that are found in municipal effluents, including nitrogen, can reduce the amount of fertilizer production, as well as decrease the loss of nutrients being discharged into the environment [30]. The last market reports (2022 as a base year) indicated that the global market size of nitrogenous fertilizers has reached $60.3 billion (30 % of the global market size of fertilizers), in which urea has alone the largest segment share (71 %; $54.4 billion) in this market [31]. Currently, urea has a value of 315 UD $/tTrading [32], which is equivalent to 158 US$/t as N, while ammonium nitrate has a value of 370 US$/t [33], which is equivalent to 124 US$/t as N.

Nitrogenous fertilizers are critical to global food security due to their application in agriculture [34], and therefore the recovery of NO_3^-, NO_2^-, NH_4^+, and ON that can be used for nitrogenous fertilizers production is necessary, where global food production needs to increase to 50 % by 2050 [35]. For this purpose, various N-rich sources are used, including human urine for direct urea recovery or, due to rapid hydrolysis of urea caused by urease enzyme that is naturally present in human urine, conversion to nitrate-based fertilizers through nitrification processes [36–38], wastewater rich in NO_3^-/NH_4^+ [39,40], landfill leachate rich in ON and NH_4^+ [41,42] and contaminated natural water sources with NO_3^- [43]. Particularly purified NO_3^-, NO_2^- and NH_4^+ can be used for the industrial production of various nitrogenous fertilizers, including anhydrous ammonia (NH_3), ammonium nitrate (NH_4NO_3), ammonium nitrite (NH_4NO_2), urea ($CO(NH_2)_2$) [38,44].

1.5. Nitrogen removal from water

Biological nitrification/denitrification [45], chemical reduction [46], electrically driven membranes, such as electrodialysis [47], and pressure-driven membranes, such as nanofiltration (NF) and reverse osmosis (RO) [48], have been used to remove N compounds from water. Biological treatment can be achieved with electrochemically active microorganisms for nitrification, to oxidize NH_4^+ to NO_3^- [49], or denitrification to reduce the N species to N_2 (gas) [50]. These processes are highly sensitive to temperature and a post-pH correction may be necessary [45]. Chemical reduction using zero-valent iron, electro- and photocatalytic methods can convert NO_3^- and NO_2^- to NH_4^+ [51–53]. In addition, photocatalytic oxidation of ON, such as urea, generates NO_3^- and NH_4^+ as the major by-products [54]. Electrodialysis can achieve up to 99 % removal of NO_3^- at higher recovery [47]. However, it is not effective in removing ON [55]. On the other hand, NF and RO have the potential to remove both charged and uncharged IN and ON species [56,57]. While RO generally demonstrates high water-solute selectivity, NF often consumes less energy and may enable solute–solute selectivity during separation, preserving beneficial minerals that RO may otherwise eliminate [58].

In membrane filtration, the recovery of NO_3^-, NO_2^-, NH_4^+, and urea from N-rich water resources is generally achieved by a pretreatment step to reject scalants/foulants, such as multivalent ions (Mg^{2+}, Ca^{2+}, SO_4^{2-}) and OM, using NF. This requires a NF stage with a low IN (or urea) retention. A subsequent RO stage is used to concentrate the NF permeate rich in IN species [59,60]. One scaling/fouling control strategy for the NF step is controlling concentration polarization (CP) by optimizing the hydrodynamics of the membrane system [61], allowing selective permeation of the N species, while rejecting multivalent ions and/or OM by NF.

1.6. Nitrogen rejection mechanisms in nanofiltration

Membrane type (pore size and surface charge density), and water chemistry (ionic strength and pH) are parameters that define the rejection of charged and uncharged solutes in NF [61,62]. With a fixed pore size, variable rejection of the charged IN species follows the order $NO_2^- > NO_3^- > NH_4^+$, which is related to the hydration energies and ultimately different degree size exclusion [63,64]. This is most particular for NO_3^- compared to NO_2^- despite these species having the same charge. The transport of IN compounds in NF can be enhanced by temperature due to the increase in the membrane pose size and reduction in water viscosity, in addition to diffusivity, hence reducing size exclusion [65]. Size (or steric) exclusion is relevant for ON rejection with NF, which principally depends on molecular weight (MW). For example, lower rejection (~ 20 %) for urea (MW 60 Da) with NF was reported [66], while 80 % rejection with NF was achieved for ON originating from OM-rich surface water [67], where the MW would be significantly higher. This reflects the role of the OM size having ON content in the water matrices and underlines the importance of adapting NF membranes to specific OM types.

Regarding charge exclusion, high rejection of the negatively charged IN species NO_3^- and NO_2^- was observed when increasing the pH, and ultimately the surface negative charge of the NF membrane [65,68]. In contrast, NF exhibits lower rejection of NH_4^+ with increasing pH [69]. Rejection of urea, a neutral ON compound across the entire pH spectrum, is not anticipated to result from charge interactions with charged NF membranes [69], while charged ON rejection by NF membranes can occur due to charge repulsion, which depends on protonation and deprotonation of the functional groups of the membrane active layer material that vary with pH [48]. Emerging studies on membrane material and process development focusing on the interplay of these rejection mechanisms could offer selective N recovery and hence applied to the N circular economy. While several studies focus on devolving selective NF membranes towards N recovery [70,71], understanding the limiting conditions of inorganic and organic N separation with existing NF membranes, which is the purpose of this work, is needed to understand the process and evaluate the required approach to maximize N recovery.

This interplay between size and charge exclusions in NF is investigated further for both IN compounds (NO_3^-, NO_2^-, NH_4^+), as well ON compounds (urea and other OM with ON content). For this, the implications of membrane pore size, charge interactions with varying pH and ionic strength, as well as the presence of different OM were investigated. The research focuses on answering three main questions: (i) evaluating the ability of NF to reject NO_3^-, NO_2^-, NH_4^+, and ON (ii) examining the influence of operating conditions and water chemistry variability (pH and ionic strength) on the rejection of the different N compounds with NF, and (iii) determining the rejection behaviour of the IN species in the presence of OM with organic nitrogen fractions. The results highlight the potential of NF as a method for improving drinking water quality in cases of both organic and inorganic nitrogen contaminations, as well as for potential N recovery.

2. Materials and methods

2.1. *Filtration system, nanofiltration membranes and operating parameters*

Filtration experiments were carried out in a crossflow filtration system with a maximum allowable working pressure of 20 bar (Fig. 1). The system components are described in detail by Boussouga et al. [72], while the filtration protocol is summarised in Table S1.

Flat sheet NF membranes, namely NF90, and NF270 from DuPont (USA), were used to compare the rejection of the different N compounds of interest. The high salt rejection of NF90 with low permeability was compared to NF270, which has high permeability and low salt rejection. The properties of these NF membranes are presented in the supporting information (Table S2).

The feed flow rate (Q_F) was fixed at 0.45 $L.min^{-1}$, corresponding to a crossflow velocity of 0.42 $m.s^{-1}$, which is within the acceptable operation range (0.05–0.5 $m.s^{-1}$) of spiral wound modules [73]. The permeate flow rates (Q_p) were fixed at 1 $mL.min^{-1}$ for NF90 and 9 $mL.min^{-1}$ for NF270 considering the water permeability of the NF membranes at 20 g.L^{-1} NaCl, as a worst-case scenario, such that the feed pressure would not exceed 20 bar. This was achieved using a proportional integral derivative (PID) controller as described by Boussouga et al. [72]. The key figures of merit were N rejection and solute permeability calculated as described in Table S3. The error analysis was evaluated based on the absolute errors for the measured quantities and the calculated parameters using Table S4).

2.2. *Chemicals and solutions chemistry*

Stock solutions of the N-compounds were prepared at 10 gN.L^{-1} from sodium nitrate ($NaNO_3$) (99.5 % ACS, Sigma-Aldrich, Germany) for NO_3^-, sodium nitrite ($NaNO_2$) (99 % ACS, Sigma-Aldrich, Germany) for NO_2^-, ammonium chloride (NaH_4Cl) (99 %, VWR, Germany) for NH_4^+, and urea (CH_4N_2O) (Ultrapure, Alfa Aesar, Germany). In the filtration experiments, the concentration of each N-compound in the feed solution was diluted to 100 mgN.L^{-1}. The structure and properties, including pKa, diffusion coefficient (D), molecular and hydrated radi, and hydration energy, of NO_3^-, NO_2^-, NH_4^+, and urea are given in Table 1, while the speciation can be found in Fig. S1.

For OM with ON content, 6 different types were selected, including

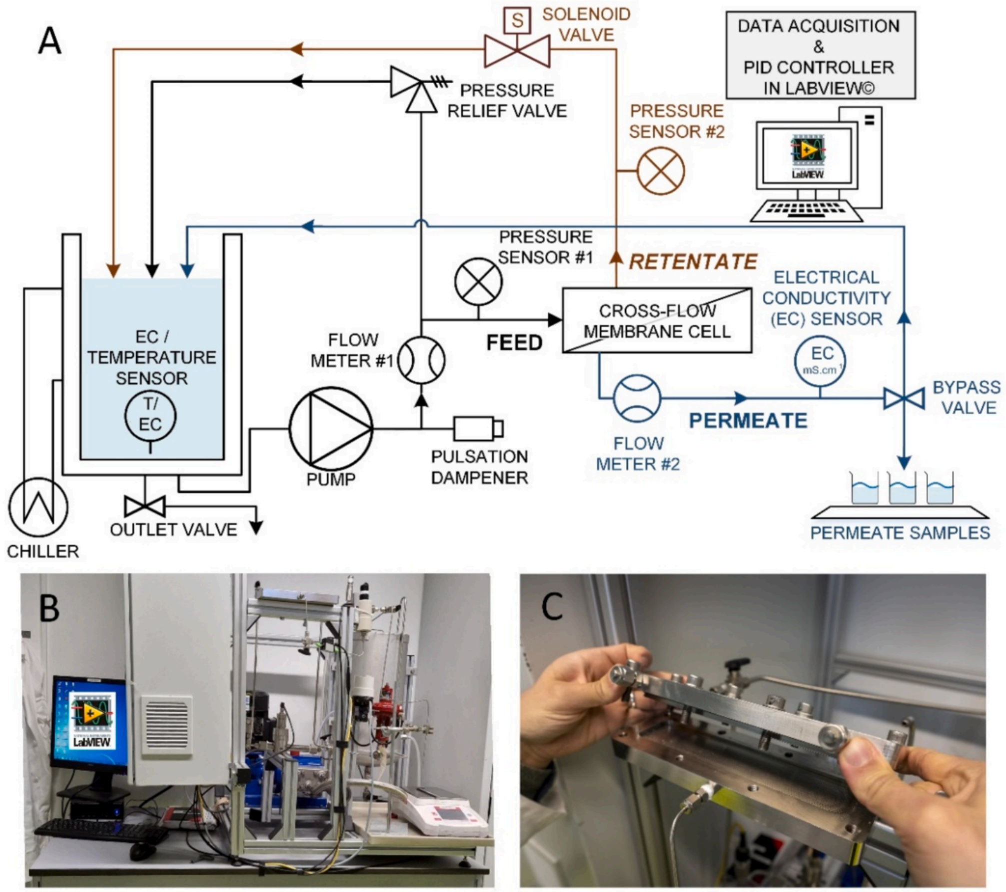
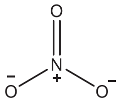
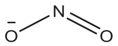
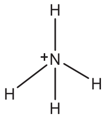
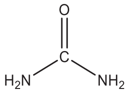


Fig. 1. (A) Schematic flow diagram and photos of (B) the cross-flow system and (C) the cross-flow filtration cell used for the NF experiments.

Table 1
Chemical structure, diffusion coefficient (D) at 25 °C, pKa at 25 °C, molecular radius (r_M), hydrated radius (r_H), and hydration energy ($\Delta H°_{Hyd}$) of the selected N-compounds.

N-compound	Structure	pKa at 25 °C [a]	D at 25 °C [b] (10^{-9} m^2/s)	r_M [c] (10^{-10} m)	r_H [d] (10^{-10} m)	$\Delta H°_{Hyd}$ [e] (kJ·mol^{-1})
Nitrate (NO_3^-)		−1.4	1.90	2.6	3.4	−314
Nitrite (NO_2^-)		3.1	1.91	1.8	3.7	−405
Ammonium (NH_4^+)		9.3	1.95	1.5	3.3	−307
Urea		0.1	1.38	1.8	2.5	−57

[a] pKa values were adapted from Haynes [90].

[b] Diffusion coefficients (D) at 25 °C were adapted from Haynes [90] for NO_3^-, $NO_2^-$and NH_4^+, and from Winkelmann [91] for urea.

[c] Molecular radii values were adapted from Nightingale [92] for NO_3^- and NH_4^+, from Iwadate et al. [93] for NO_2^-, and from Schultz and Solomon [94] for urea.

[d] Hydrated radii values were adapted from Nightingale [92] for NO_3^- and NH_4^+, from Vchirawongkwin et al. [95] for NO_2^-, and from Hawlicka and Grabowski [96] for urea.

[e] Hydration energy values were adapted from Smith [97] for NO_3^-, $NO_2^-$and NH_4^+, and from Duffy et al. [98] for urea.

humic acid (HA) (Technical®, Sigma Aldrich, Germany), tea (TATA tea, India), fermented product (FP) (Rechtsregulat Bio, Dr. Niedermaier Pharma GmbH, Germany), Australian NOM (AUS), worm farm (WF) extract, and bovine serum albumin (BSA) (Sigma Aldrich, Germany). OM origins and characteristics, including the ON content in the OM fractions, are presented in Table 2. Stock solutions (around 1000 mgC.L^{-1}) of OM matter were prepared. For powdered OM (HA, Tea, AUS), 0.5 g of the OM powder was dissolved in 500 mL of Milli-Q water (MilliQ A + system, Millipore, Germany). To enhance the solubility of HA, the solution was prepared at 4 g.L^{-1} (pellet, purity ≥ 99.9 %, Merck, Germany) and stirred for 24 h. The OM stock solutions were filtered through a 0.45 µm cellulose acetate filter (Millisart, Sartorius, Germany) to remove suspended particles and stored in a cool (5 °C) and dark place.

Table 2
The characteristics of the five organic matter compounds having organic nitrogen fractions.

Compound	Origin	MW [a] (Da)	Diameter [b] (nm)	Anionic charge [c] (µeq.L^{-1})	ON content in OM fractions [d] (%)
Humic acid (HA)	Soil	780	1.4	142.7 ± 0.3	64 % HS, 4 % BB
Tea	Plants	380	0.9	59.6 ± 0.1	64 % HS, 4 % BB
Australian NOM (AUS)	Soil	530	1.1	25.3 ± 0.1	44 % HS, 27 % BB, 26 % LMW
Fermented product (FP)	Bacterial degradation of plants	480	1.1	1.8 ± 0.2	46 % BB, 40 % LMW
Worm farm (WF) extract	Vermi-degradation of plants	17,000	7.1	115.2 ± 0.4	33 % HS, 54 % LMW
Bovine serum albumin (BSA)	Serum proteins	66,430	14.7	28.5 ± 0.2	100 % Bio

[a] Number-average mean molecular weight (MW) determined by Nguyen et al. [99] using liquid chromatography–organic carbon detection (LC-OCD).

[b] Calculated from the molecular weight (MW) using the equation $d = 4.074 \cdot 10^{-11} \cdot MW^{0.53}$, where d (m) is the diameter and MW is the molecular weight (Da) of the OM [100].

[c] Determined by Cai et al. [101] using the polyelectrolyte titration method (10 mM NaCl, 1 mM $NaHCO_3$, 15 mgC.L^{-1}).

[d] Determined by liquid chromatography–organic nitrogen detector (LC-OND) of the different OM types used in this work (Bio: biopolymers, HS: humic substances, BB: building blocks, LMW: low molecular-weight acids and neutrals).

Feed solutions were prepared at 1 mM $NaHCO_3$ (Bernd Kraft, purity ≥ 99.7 %, Germany) as a background electrolyte added from a stock solution of 50 mM (4.2 g.L^{-1}, pH 8.3 ± 0.1). The background also consisted of 0.58 g.L^{-1} (10 mM) to 20.0 g.L^{-1} (342 mM) NaCl (VWR chemicals, purity ≥ 99.9 %, Germany) added from a stock solution of 200 g.L^{-1} (3.42 M). For experiments requiring pH adjustment, 1 M HCl (Roth, Rotipuran® 37 %, Germany) and 1 M NaOH prepared from pellets (Merck Emsure® ISO, purity 99 %, Germany) were used. MilliQ water was used for the preparation of all solutions.

2.3. Water quality analysis

Ion chromatography (IC) (Metrohm 580 Professional IC, Switzerland) with an anionic column (A Supp 5, Metrohm, Switzerland) was used for the analyses of anions (NO_3^- and NO_2^-), while the cationic column (Metrosep C 4–150/4.0, Metrohm, Switzerland) column was used for NH_4^+ analysis, all with a limit of detection (LoD) of 0.4 mg.L^{-1}. Calibration curves are shown in Fig. S2.

Nitrogen concentration in the samples containing urea and OM was analyzed by liquid chromatography – organic carbon detection/organic nitrogen detector (LC-OCD/OND) (Model 9, Dr Huber DOC-Labor, Germany). Calibration curves are presented in Fig. S3. The LoD of the LC-OCD/OND method is 0.02 mgC.L^{-1} for OCD and 0.002 mgN.L^{-1} for OND published earlier by Imbrogno et al. [74]. A total organic carbon (TOC) analyser (Sievers M9. General Electric, USA) was used to determine the organic carbon content in stock solutions and water samples from the filtration experiments. The LoD of the method is 0.3 mgC.L^{-1}. Calibration curves are presented in Fig. S4.

The measurements of pH and electrical conductivity (EC) were conducted in the feed and permeate using an EC/pH meter (WTW, model pH/Cond 3320, Germany) with TetraConc® 325 (1 µS/cm – 2 S/cm, cell constant 0.475 1/cm, WTW, Germany) and SenTix™ pH-Electrode (0–14, 3 mol.L KCl, Ag$^+$ free, WTW, Germany).

3. Results and discussion

The purpose of this research was to investigate the potential of NF to reject N from inorganic (NO_3^-, NO_2^-, and NH_4^+), and organic (urea, and OM with ON content) species. Size and charge effect were elucidated on NO_3^-, NO_2^-, NH_4^+ and urea, while the implication of OM on rejection with ON content was investigated in the presence of NO_3^- and NH_4^+. The membrane type, and ultimately different membrane pore size, was the first parameter of interest.

3.1. *Rejection of nitrogen compounds by different nanofiltration membranes*

Filtration experiments with IN species (NO_3^-, NO_2^-, and NH_4^+) and the ON compound urea, at controlled flux conditions, were carried out using the cross-flow filtration system (Fig. 2). Two NF membranes (NF270 and NF90) of different water permeability, salt rejection and pore size were chosen to evaluate N-compound rejection. The stability of permeate flow rate and temperature over the filtration time is presented in Fig. S5. To achieve a reasonably constant flux of around 120 $L.m^{-2}.h^{-1}$ for NF270 and 15 $L.m^{-2}.h^{-1}$ for NF90 (Fig. 2A, B) it was necessary to vary the transmembrane pressure (TMP) between 9 – 11 bar (NF270) and 2 – 3 bar (NF90). The flux and the resulting TMP were relatively stable over the experiments. The higher pressure was chosen for the membrane with the higher permeability, to achieve an appropriately higher flux.

Rejection is low, especially for NO_3^- resulting in permeated concentration of 60–80 $mgN.L^{-1}$. Lower N concentration for the IN species in the permeate was obtained by NF90, which has a smaller pore radius (0.29 nm; Table S2) compared to NF270 (0.34 nm; Table S2) (Fig. 2C), highlighting the variable roles of size and charge exclusion with different membrane types. The rejection order of the IN species ($NH_4^+ > NO_2^- > NO_3^-$) is in agreement with the results obtained by Popova et al. [65] (Fig. 2D). NH_4^+ exhibits the highest N rejection due to the charge attraction with the negative surface charge of NF270 and NF90 at the pH conditions of the experiments (zeta potential values are –73 mV for NF270 and –52 mV for NF90 at pH 8; Table S2). This was claimed to reduce the solute permeability through the membranes, similar to most monovalent counter-ions during NF separation [75]. The higher rejection of NH_4^+ could also be a result of the difference between the hydrated radius of NH_4^+ (0.33 nm; Table 1). This radius is very close to the pore radius of NF270 (0.34 nm) and larger than the pore radius of NF90 (0.29 nm). For urea, low rejection values (below 10 %) were obtained with both NF270 and NF90. This was due to its small hydrated radius (0.25 nm; Table 1) compared to the NF membrane pore radius (0.29 – 0.34 nm; Table S2) and its neutral charge which further impedes rejection by charge exclusion.

This different removal behaviour observed by NF implies that different approaches towards N recovery are applicable depending on the N compounds. For instance, the focus on NH_4^+ recovery in the NF concentrate could be more favourable seeing the relatively high removal. This approach was indeed applied for NH_4^+ recovery for wastewater, but other components of the water matrix, such as multivalent cations (e.g. Ca^{2+}, Mg^{2+}), and other water quality parameters such as pH that enhance NH_4^+ permeation through the NF, and hence NH_4^+ recovery in NF permeate could be adopted [76]. The low removal of urea by NF implies that the recovery is only possible in the NF permeate, while other impurities, such as multivalent ions are retained by the NF, and further processes, such as RO, can be used for retaining, and hence concentrating urea [57,77]. Regarding the recovery of NO_2^- and NO_3^-, of similar rejection behaviour by NF around 20–40 %, NF can be operated in a hybrid process with RO to enhance the permeate quality while N is recovered in the RO concentrate [59].

The role of size exclusion was further elucidated when the rejection of the charged IN species by NF90 was reduced with increasing

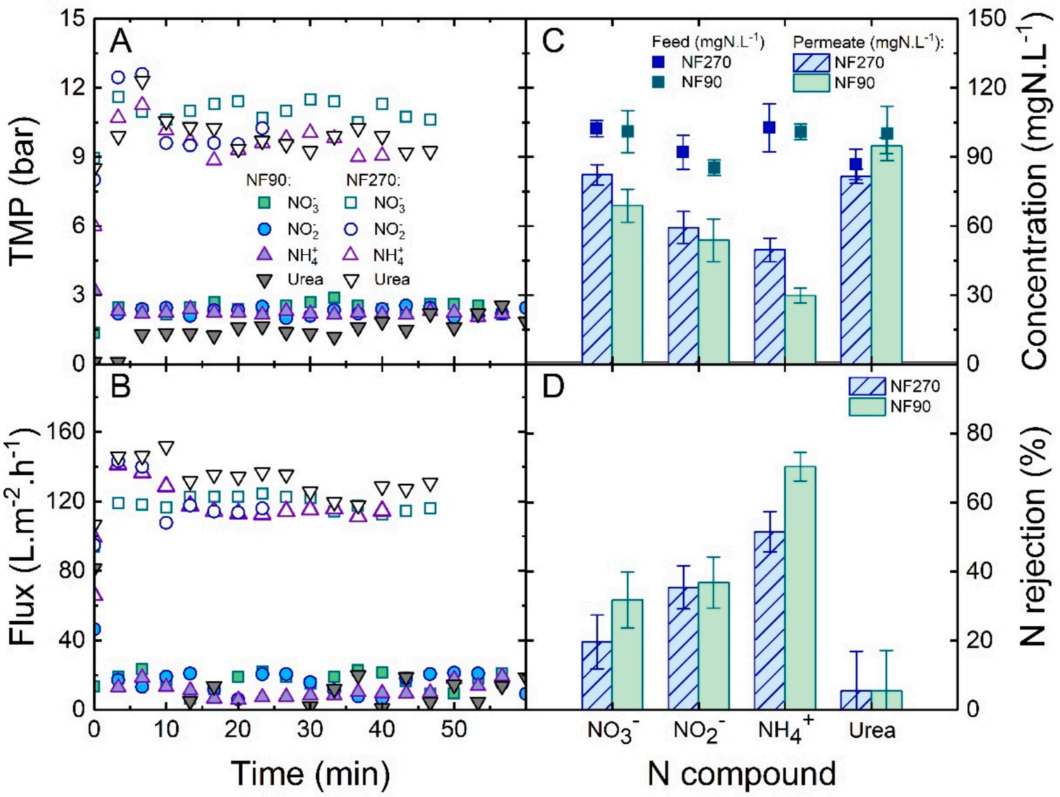


Fig. 2. (A) Transmembrane pressure (TMP) and (B) flux as a function of filtration time, as well as N concentration in permeate and feed and N rejection of the different N-compounds by NF270 and NF90 (100 $mgN.L^{-1}$, 1 mM $NaHCO_3$, 0.58 $g.L^{-1}$ NaCl, pH 8.1 ± 0.2, Q_F 0.45 $L.min^{-1}$, $Q_{P\text{-}NF90}$ 1 $mL.min^{-1}$, $Q_{P\text{-}NF270}$ 9 $mL.min^{-1}$, 24.0 ± 0.5 °C).

temperature (Fig. S6, Fig. S7). This was attributed to the increase in diffusion of IN species with potentially enlarged membrane pores [78], and decrease in water viscosity and the subsequent reduction of rejection by size exclusion. N rejection observed with NF is governed by size exclusion and charge exclusion mechanisms during the separation of charged N species (NO_3^-, NO_2^-, and NH_4^+). The role of charge exclusion was investigated by varying pH which affects N-compound speciation as well as membrane surface charge in the next section.

3.2. *Role of charge exclusion on rejection of nitrogen compounds by nanofiltration*

To evaluate the role of charge exclusion during the separation of the IN species (NO_3^-, NO_2^-, and NH_4^+) and the ON compound (urea), pH was varied from 2 to 12 and N rejection and solute permeability was investigated (Fig. 3). Supplementary data on the stability of the operating parameters (pressure, flow rate, and temperature) as well as the rejection of salinity are shown in Figs. S8 and S9.

Across the investigated pH range, N concentration in the permeate was lower when using NF90, which was expected, given the smaller pore radius than NF270 (Fig. 3A, B), even though this membrane has a more negative charge. Varying pH altered the N concentration in the permeate for the charged IN species (NO_3^-, NO_2^-, and NH_4^+) to varying degrees. The permeate concentration of urea, which is a neutral ON compound, remained consistently high.

While NO_3^- does not change ionic charge or size over the investigated pH, varying the pH from 2 to 12 resulted in a change in N rejections (Fig. 3C, D). The observed trend in rejection of NO_3^- with varying pH is in agreement with previous findings by Epsztein et al. [79], who attributed the changes to the modification of the surface charge of the NF membranes that become more negative with increasing pH. NH_4^+ and NO_2^-, which undergo deprotonation at pH 9.3 and 3.1, respectively (Table 1), the contribution of charge exclusion on N rejection and solute permeability was observed to vary with pH. The observations resulted from both speciation and membrane charge variations. N rejection of urea remained lower than 10 % regardless of the feed pH, confirming that charge exclusion does not play a role and cannot induce an increased retention.

Charge exclusion appears to be a primary mechanism for the separation of NO_3^-, NO_2^-, and NH_4^+ by NF. Changes in salinity of waters to be treated can render this mechanism ineffective due to charge screening. To evaluate the degree of such a reduction, ionic strength is investigated

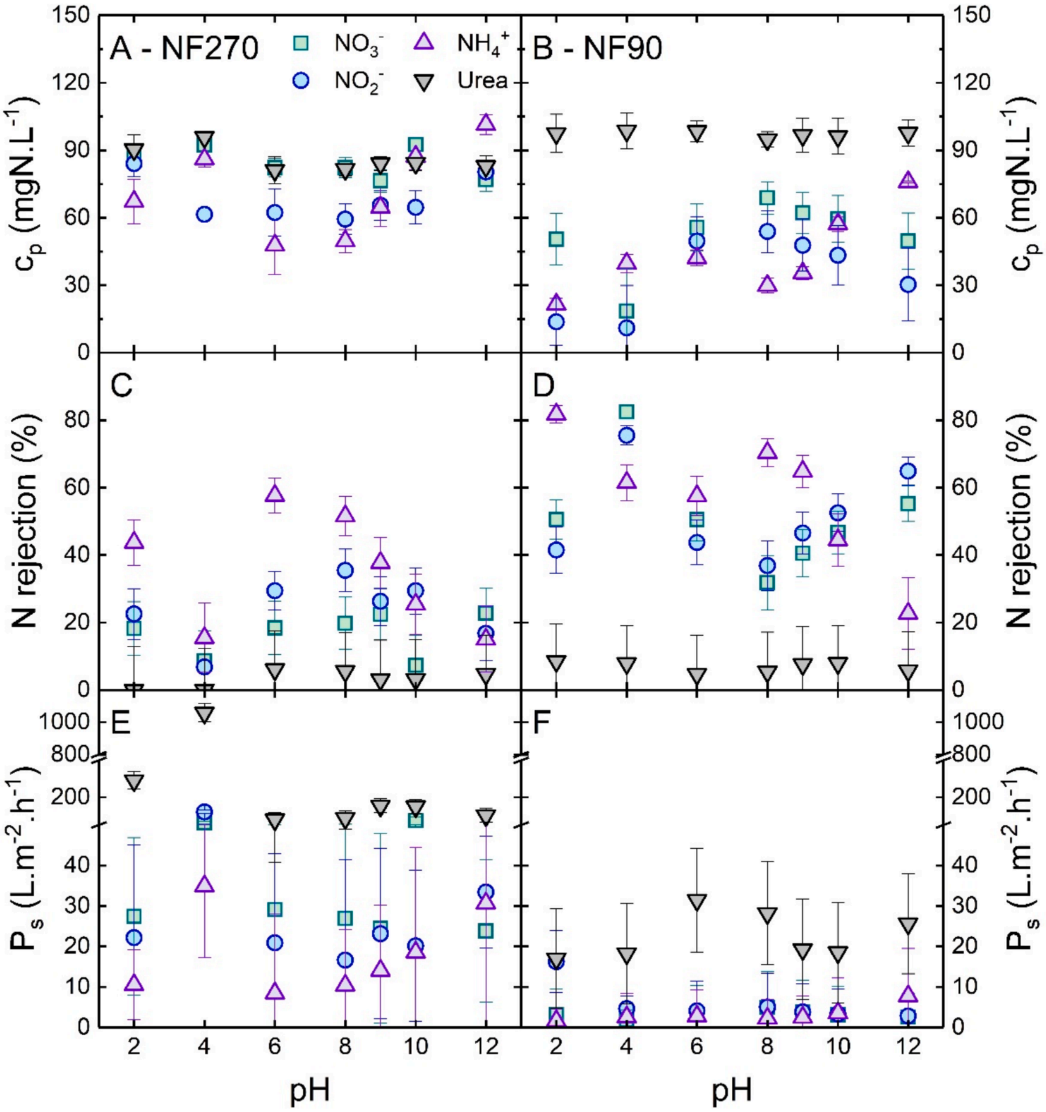


Fig. 3. (A, B) N concentration in permeate, (C, D) N rejection, and (E, F) solute permeability of the N-compounds NO_3^-, NO_2^-, NH_4^+, and urea as a function of pH during NF experiments with (A, C, E) NF270 and (B, D, F) NF90 (100 $mgN.L^{-1}$, 1 mM $NaHCO_3$, 0.58 $g.L^{-1}$ NaCl, Q_F0.45 $L.min^{-1}$, $Q_{P\text{-}NF90}$ 1 $mL.min^{-1}$, $Q_{P\text{-}NF270}$ 9 $mL.min^{-1}$, 24.0 ± 0.5 °C).

next.

3.3. Charge screening during rejection of inorganic nitrogen species by nanofiltration

Charge exclusion as a separation mechanism of ions in NF can be constrained by the ionic strength conditions, potentially leading to reduced ion rejection due to the membrane surface charge screening [80]. This has been investigated for NO_3^- and NH_4^+ by varying the ionic strength with NaCl from 0.58 to 20 g.L^{-1} (Fig. 4). Data on the stability of the operating parameters (pressure, flow rate, and temperature), water permeability, and salinity rejection can be found in Fig. S10.

For both NF270 and NF90, increasing NaCl concentration from 0.58 to 5 g.L^{-1} decreased the rejection of NO_3^-, while no further decrease was observed from 5 to 20 g.L^{-1} (Fig. 4A). This aligns with the charge screening behaviour of these particular membranes (NF270 and NF90) that only occurs at NaCl concentration $\leq$ 5 g.L^{-1} NaCl, while beyond this concentration ($\geq$5 g.L^{-1} NaCl) the membranes retain the negative surface charge with no further charge screening effects [81], even though at these ionic strength conditions the Debye length decreases from 3.04 nm (at 0.58 g.L^{-1} NaCl) to 0.58 nm (at 20 g.L^{-1} NaCl) [72].

In contrast, a decrease in rejection of NH_4^+ was observed over the NaCl concentration range of 0.58 to 20 g.L^{-1} (Fig. 4B). For this behaviour with NH_4^+, the charge screening would reduce the charge interaction (attraction in this case) between NH_4^+ and the negative entities of the membrane polymer (on the surface and within pores), hence increasing the intrapore diffusion that depends on charge interactions [82]. The above discussions apply equally to the behaviour of the solute permeability of NO_3^- and NH_4^+ that increased with NaCl concentration. NF270, in particular, exhibited a higher increase in solute permeability compared to NF90, highlighting the role of membrane pore size on the size exclusion mechanism for NH_4^+ separation.

The separation of both NO_3^- and NH_4^+ with NF relies on charge exclusion, where size exclusion appears to be a more significant contributor in the case of NH_4^+. Membrane surface charge modification through adsorbed charged organic matter, such as HA [83], can disrupt the electrostatic interactions and consequently the rejection of ions. The following sections explore this phenomenon.

3.4. Implication of organic matter on inorganic nitrogen rejection by nanofiltration

The potential implication of organic matter on the separation of NO_3^- and NH_4^+ with NF was investigated through N rejection and solute permeability at different HA concentrations (0 to 100 mgC.L^{-1}, see Fig. 5). Given charge exclusion matters for NO_3^- and NH_4^+ separation and OM is bound to alter the surface charge modification, the rejection of NO_3^- and NH_4^+ may vary. Supplementary data on the stability of the operating parameters (pressure, flow rate, and temperature), water permeability, and TOC rejection are reported in Fig. S11.

The impact of OM is relatively minor. For NO_3^-, the N rejection increased by up to 20 % for NF270 upon the addition of $\geq$ 25 mgC.L^{-1} HA, while a $\leq$ 10 % increase was observed with NF90 with 5 mgC.L^{-1} (Fig. 5A). Seeing HA and NO_3^-, are both negatively charged at the pH condition of the experiments, complexation is not an option. The reason for the small increase in rejection may be membrane surface charge modification. Previous investigations revealed that in the presence of HA, the surface charge of NF270 and NF90 becomes more negative [84–85]. This behaviour arises from the adsorption of HA on the membrane surface, which introduces further negatively charged entities, such as deprotonated carboxylic acids [83].

The changes for NH_4^+ were equally minor. The presence of HA $\geq$ 5 mgC.L^{-1} increased N rejection by up to 10 % (Fig. 5B). While solute–solute interactions between HA, which has an anionic charge of 142.7 μeq.L^{-1} at 15 mgC.L^{-1} (Table 2), and NH_4^+ could be one explanation, such electrostatic interactions between HA and the monovalent

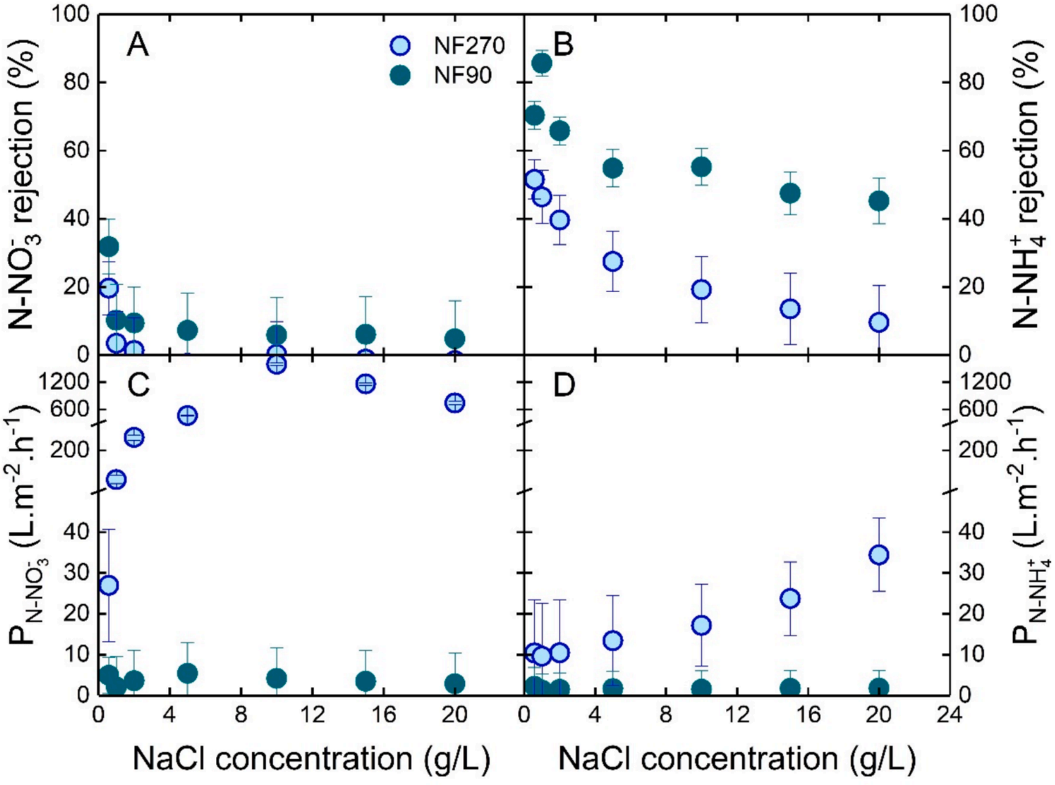


Fig. 4. Rejection of (A) N-NO_3^- and (B) N-NH_4^+, as well as the solute permeability of (C) N-NO_3^- and (D) N-NH_4^+ as a function of NaCl concentration during NF experiments with NF270 and NF90 (100 mgN.L^{-1}, 1 mM $NaHCO_3$, pH 8.1 ± 0.2, Q_F0.45 L.min^{-1}, $Q_{P\text{-}NF90}$ 1 mL.min^{-1}, $Q_{P\text{-}NF270}$ 9 mL.min^{-1}, 24.0 ± 0.5 °C).

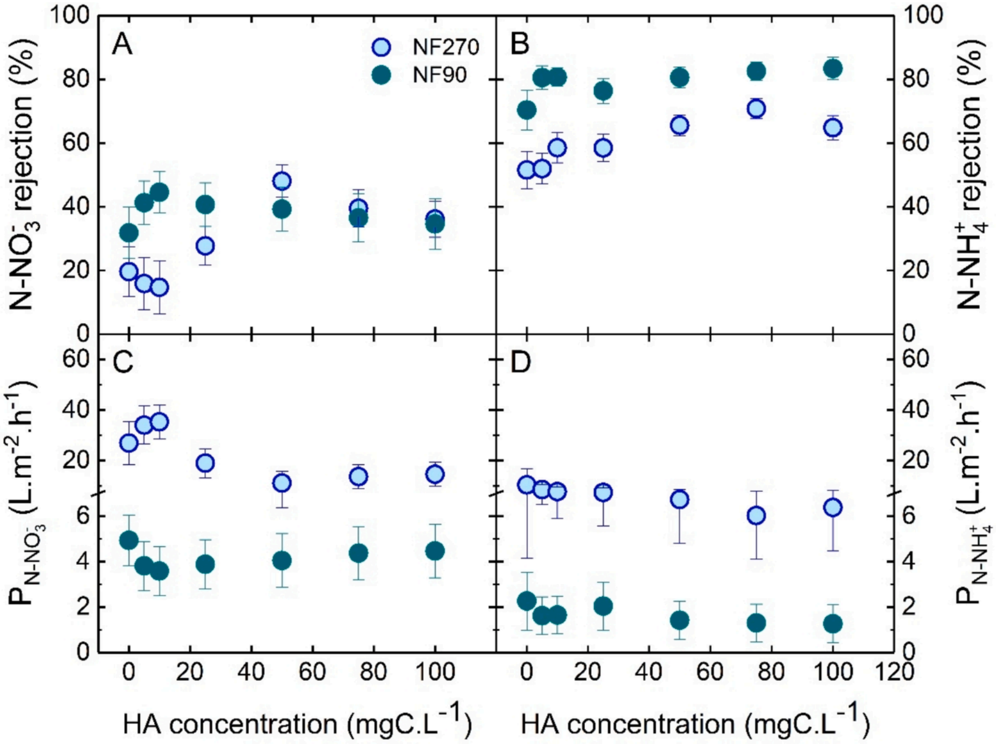


Fig. 5. Rejection of (A) $N\text{-}NO_3^-$ and (B) $N\text{-}NH_4^+$, as well as the solute permeability of $N\text{-}NO_3^-$ and (D) $N\text{-}NH_4^+$ as a function of HA concentration during NF experiments (100 mgN.L^{-1}, 1 mM $NaHCO_3$, 10 mM NaCl, pH 8.1 ± 0.2, Q_F0.45 L.min^{-1}, $Q_{P\text{-}NF90}$ 1 mL.min^{-1}, $Q_{P\text{-}NF270}$ 9 mL.min^{-1}, 24.0 ± 0.5 °C).

cations are considered weak and unstable [86]. At the lowest investigated HA concentration (5 mgC.L^{-1}), the equivalent anionic charge is 47.6 μeq.L^{-1}, which is approximately seven times higher than the cationic charge from $N\text{-}NH_4^+$ in the feed solution (100 mgN.L^{-1} equivalent to a cationic charge of 7.1 μeq.L^{-1}). The second reason for the small increase in $N\text{-}NH_4^+$ rejection could be due to the condition of electrical neutrality in the feed solution, when co-ions rejection (such as Cl^-) increased in the presence of HA, in addition to the high rejection of

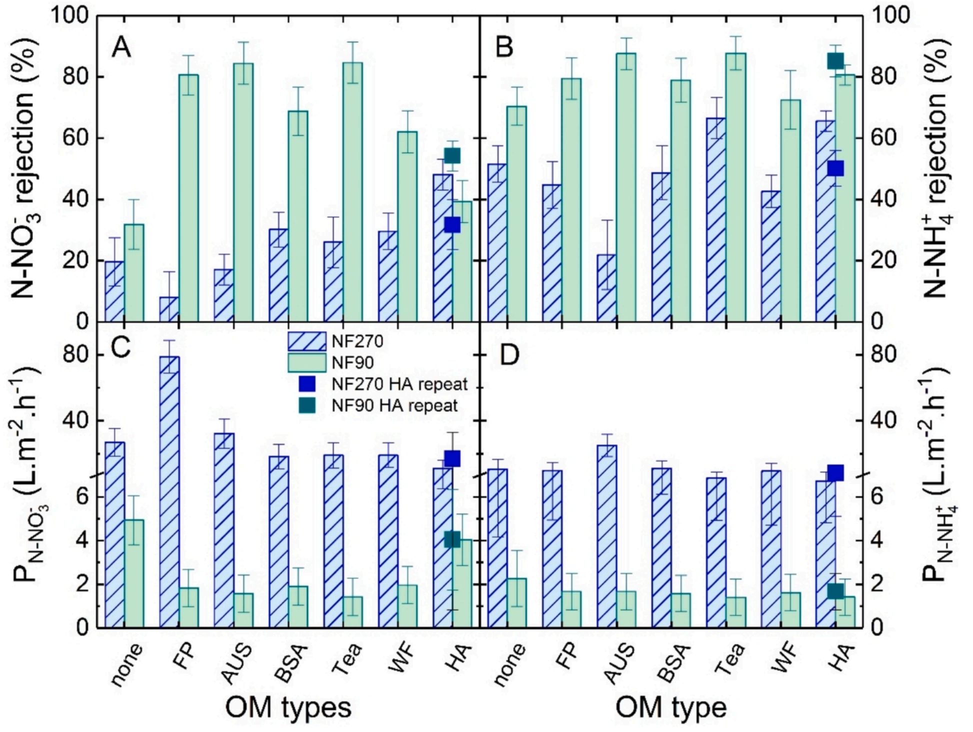


Fig. 6. Rejection of (A) $N\text{-}NO_3^-$ and (B) $N\text{-}NH_4^+$, as well as the solute permeability of (C) $N\text{-}NO_3^-$ and (D) $N\text{-}NH_4^+$ as a function of OM types (100 mg.L^{-1} as N, 1 mM $NaHCO_3$, 10 mM NaCl pH 8.1 ± 0.2, 50 mgC.L^{-1} OM; Q_F 0.45 L.min^{-1}, $Q_{P\text{-}NF90}$ 1 mL.min^{-1}, $Q_{P\text{-}NF270}$ 9 mL.min^{-1}, 24.0 ± 0.5 °C). The OM types in the x-axis are ordered by their anionic charge.

HA (80 – 99 %, Fig. S11) with negatively charged entities. The condition of the electrical neutrality in NF is commonly used to explain the rejection of a mixture of co-ions/counter-ions with different charge valencies [87], and could be a plausible explanation in this case if major changes were observed. Instead, it appears that rejection and solute permeability are reasonably constant over an extremely large range in HA concentrations.

The solute permeability of N-NO_3^- and N-NH_4^+ was determined based on the experimental rejection and the concentration at the membrane surface calculated from the film-theory. A minor decreasing trend in presence of HA (Fig. 5C, D) is within error. Such a trend would highlight that the presence of HA induces an additional barrier against the permeance of the charged IN species most likely by enhancing the charge exclusion mechanism, but the observation is not significant.

The presence of various types of OM, each potentially carrying different anionic charges, may differently affect the rejection of N-NO_3^- and N-NH_4^+ by NF. This is examined in the following section.

3.5. *Implication of the organic matter type on inorganic nitrogen rejection by nanofiltration*

The role of OM types, particularly the impact of different anionic charges resulting from different densities and types of the acidic functional groups, on the separation of N-NO_3^- and N-NH_4^+ by NF was investigated in the presence of HA, BSA, WF, FP, AUS (Fig. 6). The OM concentration was fixed at 50 mgC.L^{-1}. TOC rejection of the different OM types is reported in Fig. S12.

For NO_3^-, the presence of BSA, Tea, WF, and HA at a concentration of 50 mgC.L^{-1} enhanced N rejection by NF270. In the case of NF90, a more significant increase in N-NO_3^- rejection was observed, regardless of the OM type (Fig. 6A). NF270 showed a trend of increasing N-NO_3^- rejection with increasing OM anionic charge, whereas this relationship was not observed with NF90. For NF270, at least, this could explain that OM with a high anionic charge enhances the charge exclusion mechanism for the rejection of N-NO_3^- by NF. Although initial experiments on N-NO_3^- rejection in the presence of HA showed higher rejection with NF270 compared to NF90, repeated trials aligned with the trend that the tight membrane (NF90) achieved better rejection. This was also the case of N-NH_4^+ rejection in the presence of HA, where NF90 exhibited higher N rejection compared to NF270 (Fig. 6B). Regarding N-NH_4^+, the presence of FP and AUS, which have the lowest anionic charge compared to other OM types, reduced the rejection in the case of NF270, while only the presence of Tea and HA induced a measurable increase in the rejection (Fig. 6B). With NF90, the rejection of N-NH_4^+ has generally increased in the presence of OM regardless of the OM type (Fig. 6B).

FP increased the solute permeability of N-NO_3^- (Fig. 6C). This could be due to the simultaneous transport of NO_3^- and FP, which has a low MW (480 Da) and a low anionic charge (1.8 μeq.L^{-1}), in addition to the generally low rejection exhibited by NF270 (Fig. S12). Such a joint transport is a requirement to conserve the electroneutrality across the membrane pores [88]. With NF90, which has a high rejection of the different OM types (Fig. S12), the solute permeability of N-NO_3^- was reduced significantly regardless of OM type (Fig. 6C). The transport of N-NH_4^+, on the other hand, was not affected by the OM type when using both NF270 and NF90 (Fig. 6D). In summary, the rejection of N-NO_3^- and N-NH_4^+ could be increased in the presence of OM, while the anionic charge and the size of the OM were more relevant to the transport of NO_3^- through NF membranes.

While the OM retention is high, the ON rejected by the NF membranes will be investigated last to evaluate the selectivity that can be achieved between IN and ON.

3.6. *Separation of organic nitrogen fractions in organic matter by nanofiltration*

The separation of ON, contained in OM, may depend on the membrane pore size, as well as the size and the anionic charge of the OM. Low rejection was shown for low MW urea with NF. To investigate the ON in the OM fractions rejected by NF, LC-OCD/OND analysis was performed (Fig. 7).

In the first instance, the presence of ON in OM was confirmed with OND signals of different intensities depending on the OM type with a distribution following the OM fractions shown by the OCD signals. The large OND signals observed between 35 – 50 min retention time corresponds to NO_3^- in the feed solution, which is not taken into account when discussing the OND signals.

In NF, the OND and OCD signals in most of the permeate samples of the different OM types by NF270 and NF90 were significantly reduced compared to the OND and OCD signals in the feed. This confirms rejection of the different OM, even though this was comparatively low in the case of FP (Fig. S12). For HA (Fig. 7A), the ON is found in the region of HS and BB with a similar OND signal compared to Tea (Fig. 7B), but a lower OND signal compared to AUS (Fig. 7C), and WF (Fig. 7E). The ON in these OM was completely rejected by NF membranes since no OND signal for the permeate samples could be detected. In the case of BSA (Fig. 7D), which has the highest molecular diameter (14.7 nm; Table 2) compared to the other OM types and contains a large fraction of N ($C_8H_{21}\mathbf{N}OSi_2$), an OND signal was observed in the biopolymer region, where most of the ON fractions were rejected by NF. For FP (Fig. 7F), which contains LMW OM fractions, the OND signal may have interfered with the signal of NO_3^- in the feed solution, and for this reason, the ON signal of FP in the feed and permeate could not be quantified.

In summary, the rejection of ON content in OM fractions is higher with NF membranes, emphasizing the potential of NF technology to the circular nitrogen economy of wastewater rich in OM, where water recovery can be achieved simultaneously. The separation of the IN species by NF revealed that NH_4^+, which is commonly found in urban wastewater and landfill leachate, had the highest rejection, and the approach of concentrating by NF is more reasonable. The low rejection of urea by NF, due to its neutral charge, on the other hand, can be subsequently coupled with RO where higher rejection could be achieved.

The findings have clear economic benefits, by demonstrating the potential of NF to contribute to the circular economy frameworks of nutrients and water recovery by addressing both organic and inorganic nitrogen contaminants. In this context of N circular economy, NF can be integrated into agriculture, in which N in both organic and inorganic forms can be recovered from N-rich water sources and reused as fertilizers while achieving water reuse for irrigation. For this, N recovery by NF can be applied in various N-rich sources such as human urine followed by conversion to nitrate-based fertilizers through nitrification processes [36–38], urban wastewater rich in NO_3^-/NH_4^+ [39,40], and contaminated natural water sources with NO_3^-, in which NO_3^- is captured and converted through reduction processes to NH_4^+ [43].

Considering the market value of N fertilizers, particularly urea (343 UDS/tTrading [32]), and ammonium nitrate (370 UDS/t [33]), and the critical importance of N fertilizers to global food security due to their application in agriculture [34], the findings on N recovery with NF are of important value. In parallel to N recovery, combining NF with other processes, such as RO, coagulation, ion exchange, and adsorption, can provide opportunities for the targeted permeate quality that can fulfill the water reuse criteria of different industries [89].

4. Conclusions

The objective of this study was to investigate the rejection of various N-compounds, including NO_3^-, NO_2^-, NH_4^+, urea, and OM with ON content by nanofiltration, focusing on the contributions of different separation mechanisms. Positively charged IN species such as NH_4^+ had the highest rejection compared to NO_2^- and NO_3^-, while urea, a neutral N-compound, showed the lowest rejection (below 10 %). Size exclusion was elucidated when comparing the rejection exhibited by NF membranes of different pore diameters. Varying pH and ionic strength,

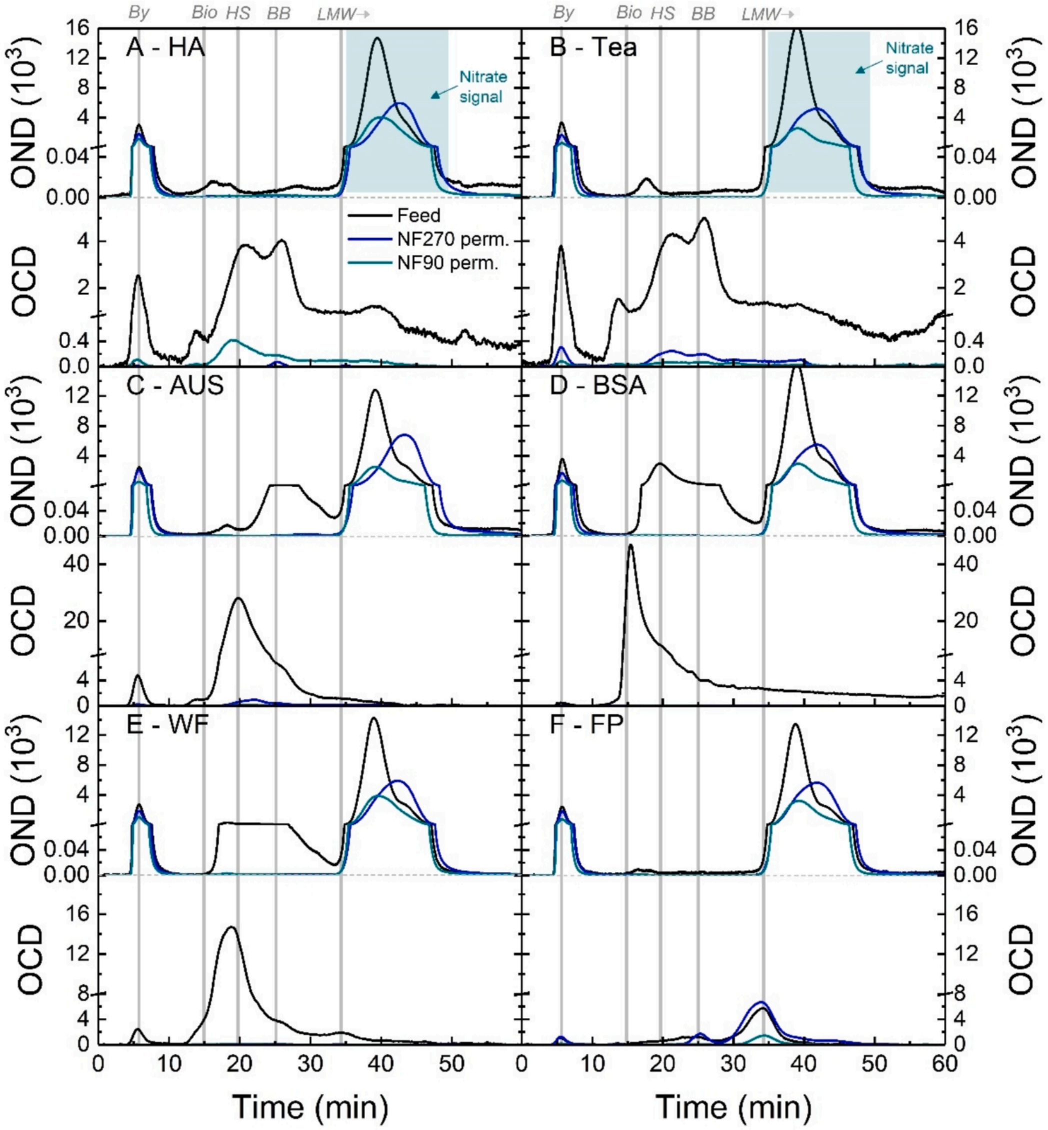


Fig. 7. OND and OCD signal response of (A) HA, (B) Tea, (C) AUS, (D) BSA, (E) WF, and (F) FP in feed and permeate samples of NF270 and NF90. (100 mg.L^{-1} as N, 1 mM $NaHCO_3$, 10 mM NaCl pH 8.1 ± 0.2, 50 mgC.L^{-1} OM; Q_F 0.45 L.min^{-1}, $Q_{P\text{-}NF90}$ 1 mL.min^{-1}, $Q_{P\text{-}NF270}$ 9 mL.min^{-1}, 24.0 ± 0.5 °C). The term By stands for bypass.

revealed that charge exclusion is an important mechanism for the rejection of charged nitrogen species (NO_3^-, NO_2^-, and NH_4^+), while the separation of urea, a neutral N-compound, was limited to size exclusion and could not be retained.

The presence of OM with a concentration up to 50 mgC.L^{-1} enhanced the rejection of NO_3^- and NH_4^+ by NF likely due to enhanced charge exclusion, and the OM of high anionic charge density caused the most significant increase in NO_3^- and NH_4^+ rejection. The ON in the studied OM, of different molecular diameters (0.9 – 14.7 nm) and anionic charge (1.8 – 142.7 μeq.L^{-1} at 15 mgC. L^{-1}), particularly in biopolymer and humic substances fractions, were rejected by the NF membranes.

The findings highlight the potential of NF as a method for both improving water quality and nitrogen recovery from organic and inorganic nitrogen contaminations. The drive towards a nitrogen circular economy requires higher fertilizer efficiency, thus a lower application of nitrogen compounds and enhanced natural nitrogen fixation. This will result in more nitrogen compounds in soil and water, along with the recovery and reuse of wasted nitrogen, which is of concern when useful nitrogen compounds can be recovered and reapplied. This requires effective separation processes for water supplies and wastewater reuse, and here NF could be integrated.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2025.132552.

Supplementary data related to this article is available in the supporting information (SI) section. The SI contains further results as figures with some comments regarding (i) the filtration protocol, (ii) membrane characteristics, (iii) speciation of the charged nitrogen species, (iv) data and error analysis, (v) calibrations of the analytical instruments (IC, TOC, LC-OCD/OND), and (vi) supplementary data for the filtration experiments.

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