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Effects of High Concentrations of Organic and Inorganic Pollutants in Waste Water and Drinking Water on Nanofiltration Membrane Behavior

Nikoleta Kukučka Stojanović and Miroslav Kukučka

Additional information is available at the end of the chapter

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Abstract

Removal possibility of high concentrations of organic and inorganic matter from aquatic solution using “Crossflow” spiral wound nanofiltration membranes was investigated on a self-made semi-industrial pilot plant, capacity 800 L/h. Natural organic matter, ammonia ions, and total arsenic removal were examined using concentrates—waste water obtained from industrial nanofiltration plant. Nanofiltration of waste water provided conclusions that arsenic was better removed in higher organic concentration environment rather than in lower. Also, membranes removed organic carbon with high efficiency and produced drinking water quality permeate. Removal of high concentrations of total iron, manganese, calcium, and magnesium was conducted using natural groundwater with and without the presence of complexing agent. Obtained results show that molecular weight cutoff, as well as quantity and type of complexing agent, had an influence on measured parameter removal. Also, electrostatic forces influenced separation of investigated ions.

Keywords: organic matter, arsenic, metal ions, complexing agent, asymmetric polyamide nanofiltration membranes

1. Introduction

Nanofiltration (NF) is a widely used type of membrane process in the world for undesirable constituents' removal from various types of water due to its characteristic pore size that is between ultrafiltration (UF) and reverse osmosis pore size. Besides, NF membranes operate with no phase change and typically have high rejections of multivalent inorganic salts

and small organic molecules at modest applied pressures [1]. This chapter is dedicated to better understanding of nanofiltration membrane process in order to further resolve waste water treatment problems, especially waste water from nanofiltration plants. The aim of this investigation was to examine the behavior of nanofiltration membranes when exposed to high concentrations of natural organic matter (NOM) and arsenic originated from waste water. Additionally, nanofiltration process was monitored in the presence and absence of complexing agent in the environment of elevated iron, manganese, calcium, and magnesium ion concentrations originated from well water. The highlight of this work can be presented in the way that no model solution was used and that nanofiltration membranes were tested in situ allowing precise deduction and report of complex removal mechanisms that undergo in nanofiltration process. Natural drinking water resources are continuously reducing, and with regard to increasing demand for clean drinking water, it presents a great problem for the society. Large amounts of waste water are produced during drinking water production using membrane processes. The goal of waste concentrate treatment using membrane processes is firstly protection of natural drinking water resources. Nanofiltration concentrate discharge presents great problem in the means of quantity and quality. Even though NF membrane's characteristics such as materials, resistance, and efficiency are quickly improving [2–4], the question of NF concentrate discharge into the environment is still present. NOM and arsenic found in water present great problem all around the world. Elevated concentrations of NOM expressed as dissolved organic carbon (DOC) can be found in natural water in concentrations of 2.3 up to 11.90 mg DOC/L [5–9]. DOC-elevated content can also be found in waste water originated from technological processes for organic matter removal from aquatic influents [10] or in municipal waste water with up to 51 mg/L of total organic carbon (TOC) [11]. Arsenic is usually found in natural water in concentrations of 1–2 $\mu\text{g/L}$ [12]; however, several countries such as Bangladesh [13, 14], China, the USA, and Taiwan [15] can be excluded from this statistics because arsenic content in these countries in great deal exceeds maximum tolerable value determined by the World Health Organization in drinking water of 10 $\mu\text{g/L}$ where Argentina is the country with largest reported arsenic content in groundwater with up to 7550 $\mu\text{g/L}$ [16]. Nanofiltration is especially suitable for arsenic and NOM removal from different types of natural water in the process of drinking water preparation [17, 18]. Survey of previous investigations has shown that nanofiltration [19, 20] can successfully be used for arsenic removal under normal or higher pressures [21]. Besides, addition of lime to nanofiltration of NF and reverse osmosis concentrates secured arsenic concentration of less than 10 $\mu\text{gAs/L}$ in the permeate [22]. Also, it has been reported that arsenic removal efficiency is higher in the presence of humic acid [23]. Nanofiltration can be used for arsenite and arsenate removal with size exclusion [24] in molar mass range of 200–2000 Da. Electrically charged particles, especially anions, with the process of electrostatic repulsion is typical for NF membranes [25]. Pentavalent arsenic removal is significantly larger than As^{3+} , 95% and 20–50%, respectively [26, 27]. Arsenic in organic form can be removed from water with greater efficiency than nonorganic arsenic. It is found that arsenic in natural organic matter-rich environment has the ability to form complex chemical compounds with NOM anions as ligands [28]. Natural water NOM has significant influence on arsenic compound reduction and complexing [29]. Examinations of ionic force and NOM concentration influence on As(V) removal using four types of NF membranes under different transmembrane pressures (TMP) were conducted [30].

Results have shown that TMP, NOM, and several other ions' presence has an influence on arsenic removal efficiency. The degree of arsenic removal depends on organic matter concentration because the permeate flux is smaller when humic matter content is greater [30]. Secondary NF treatment of concentrate from nanofiltration plant for groundwater filtration from the city of Kikinda and Zrenjanin region has shown that large concentrations of NOM and arsenic can be removed with high efficiency [31]. It is reported in many studies that iron, manganese, calcium, and magnesium can be found in natural and waste water around the globe. Iron can be found in groundwater in concentrations smaller than 1 mg/L as well as >1 mg/L, and those are called "macro" concentrations [32]. Extremely high iron and manganese content found in the literature was in Vietnam (48 mg/L) [33] and in Cambodia (3.1 mg/L) [34], respectively. Water hardness may cause many problems in the means of calcium carbonate and magnesium hydroxide precipitation, especially in hot water systems [35–37]. Water hardness can be removed with traditional methods like ion exchange resins and lime softeners and membrane processes like electrically charged NF membranes [38, 39].

It is known that metal chelates can be successfully removed from aquatic medium using membrane processes. Membrane process technologies are proven suitable for metal separation from corresponding chelate ligands from waste water treatment-originated compounds [40]. In addition, gadolinium (III) and lanthanum (III) ethylenediaminetetraacetic acid (EDTA) complexes were successfully concentrated using nanofiltration [41].

Investigations of manganese and humic acid removal with nanofiltration have shown manganese retention from 45 to 96% with regard to pH value and HA removal efficiency of 80%. Manganese removal efficiency is the best in pH value range of 10–12. Complexation model has shown that when pH value is larger than 7, complexes of Mn and humic matter are created [42]. A group of authors has investigated combined UF-NF process for dissolved organic pollutant removal from River Huangpu in China. Turbidity, iron, manganese, and large molar mass NOM were removed using ultrafiltration, while NF process was used for smaller molar mass NOM and inorganic salt removal. Manganese and iron ion concentration in river water were up to 0.72 mg/L and up to 5.5 mg/L, respectively, while UF and NF effluents contained 0.01–0.1 mg Mn/L and 0.001–0.07 mg Mn/L, as well as 0.01–0.12 and 0.01–0.03 mg Fe/L, respectively [43]. Investigations have shown that spring water containing low iron (0.09–0.26 mg/L) and manganese (0.05–0.1 mg/L) content in the presence of NOM (2–34 mg TOC/L) can be successfully treated with nanofiltration [44]. Oxidation, coagulation, flocculation, and sedimentation can be used as UF and NF pretreatments for water that contains iron and manganese [45]. NF is also proven as a promising technique for removal of large manganese quantities from mine waste water. Dissolved manganese concentration of 115 mg/L in waste water was reduced in the permeate for 98% [46].

2. Materials and methods

Investigations of NF membrane behavior when exposed to large quantities of organic and inorganic pollutants from aqueous solution were conducted on a self-made semi-industrial

pilot plant (PNF). NOM, arsenic, and ammonium ion originated from industrial NF plant waste water concentrate and removal possibilities of stated pollutants were examined in NF-CP experiments. NF-WP experimental series was conducted for membrane behavior investigations when exposed to high concentrations of calcium, magnesium, total iron (Fe_T), and manganese originated from natural groundwater. Main components of the PNF are presented in **Table 1**. All presented components of industrial pilot plant were identical for both experiments. Only difference was chemical dosing device (DP) installed for NF-WP experimental series. Schematic of the PNF used in the experiment series NF-CP and NF-WP is given in **Figure 1A** and **B**, respectively.

2.1. NF membrane configuration

Nanofiltration membranes retain substances with molar masses higher than ~ 300 g/mol (300 Da) and multivalent ions [47]. Retention characteristics depend on the membrane type and the amount of free volume in the membranes that is most commonly influenced by flux. As the flux increases, retention of the membrane is decreased. Membrane surface can obtain surface charge via different mechanisms such as surface functioning group ionization, ion adsorption from the solution and polyelectrolyte, ion surface matters, and charged molecule adsorption [48]. Aromatic composite thin-film membranes that are used in this paper can contain carboxyl and amino functional groups [49]. Membrane surface can be positively charged in the low pH environment, as well as transformed to negatively charged with pH value rise [48].

Component	Characteristics	Manufacturer
Microfilter for inlet water pretreatment	Polypropylene filter cartridge of 5 μ m with housing	"Atlas"
Booster pump	Centrifugal multistage pump CR1-23; Q = 1.8 m ³ /h; H = 104 m	"Grundfos"
Nanofiltration modules	NF membranes $\Phi = 0.102$ m; L = 1.02 m	"Torey-Korea Inc"
Instantaneous inlet water, permeate and concentrate flow meter	Polysulfone rotameter F1 300–3.000 L/h F2 and F3 200–2.000 L/h F4 100–1.000 L/h	"IBG-Praher"
Water pressure meter	Pressure gauge 0–10 bar (M1, M2 and M5) 0–20 bar (M3 and M4)	"Wika"
Solenoid valve	EV220A NC; 3/4"	"Danfoss"
Dosing pump for chemicals dosage	Dosing pump DDC 6-10	"Grundfos"
Electric control unit	Programmable logic controller (PLC)	"Omron"

Table 1. Main components of nanofiltration pilot plant.

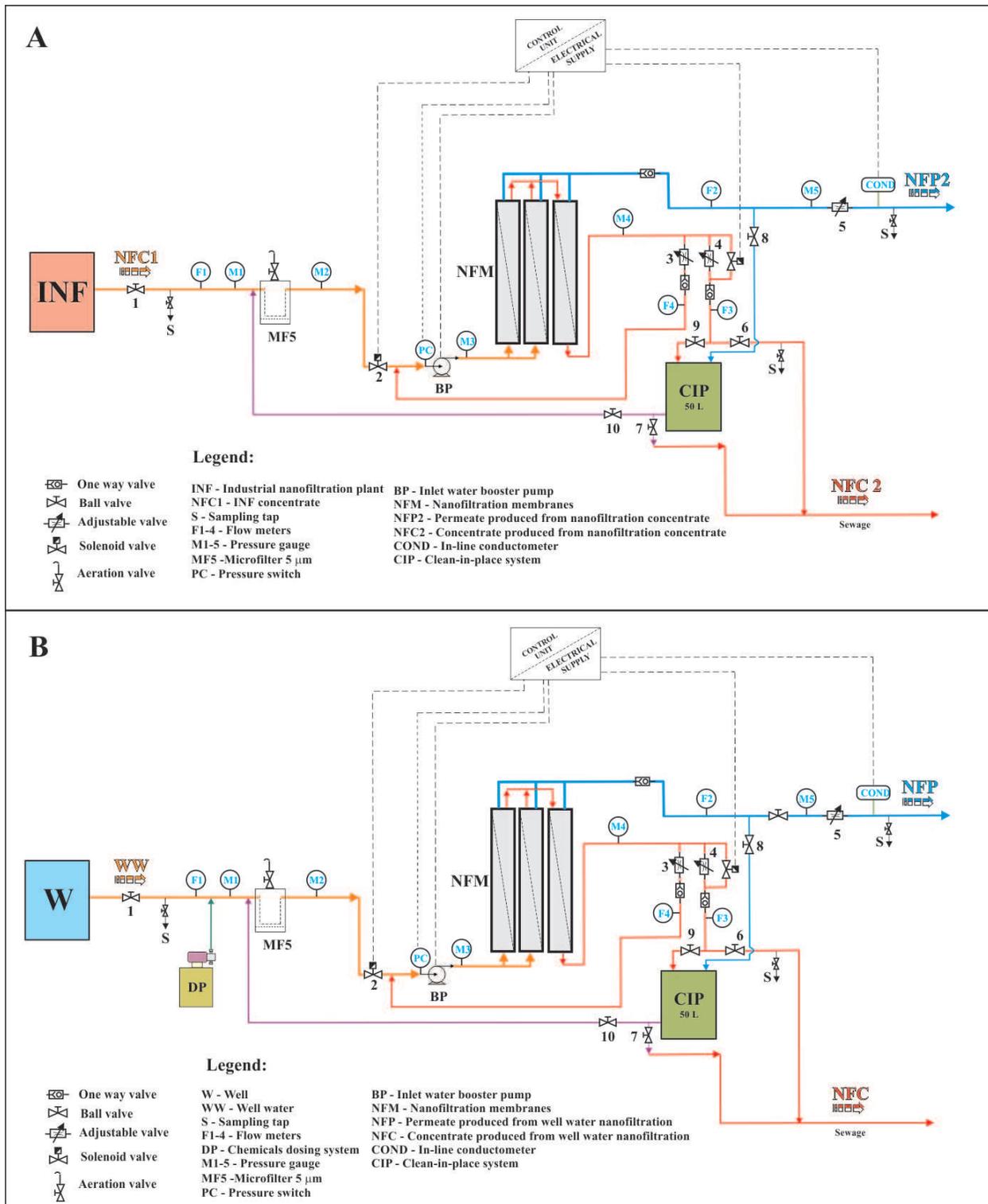


Figure 1. Pilot plant schematic diagram used in NFCP experiment series (A) and NFWP experimental series (B).

For the purpose of examination of membrane behavior, commercial spiral-wound membranes, manufacturer Toray Chemical Korea Inc., type CSM-NE 4040-70 (NE70), and CSM-NE 4040-90 (NE90) were chosen. Membrane type CSM-NE 4040-70 removes approximately 70%

and modules CSM-NE 4040-90 ~ 90% of all inorganic dissolved substances from water solution. Data obtained by the manufacturer show that membranes NE70 and NE90 possess different pore sizes and substance removal capabilities (molecular weight cutoff, MWCO). NE70 membrane type can remove substances with molar mass larger than 250 [50], i.e., 350 Da [47], while NE90 membranes remove molecules with molar mass larger than 200 Da [51]. Membrane MWCO represents molecular molar mass that can be removed using distinct type of membrane in the percentage of 90% [52]. MWCO concept is based on the constation that molecule size grows with molar mass increase [53], and MWCO shows membrane retention characteristic prediction through separation mechanisms by size [54]. PNF was designed as two-stage membrane filtration, and different, theoretically possible, combinations of NE70 and NE90 membranes were used in the NFWP experiment (**Table 2**). MWCO value for the first membrane configuration was calculated from NE 4040-70 and NE 4040-90 membrane data sheets. Pilot plant contained three membranes, two in the first stage and one membrane in the second stage. Three NE90 membranes were used for NFCP concentrate filtration experiments.

2.2. NFCP experiment series

NFCP experiment series were conducted on two locations:

- Public pool complex, J.P. "Sportski objekti," Zrenjanin (BZR)
- Public pool complex, S.R.C. "Jezero," Kikinda (BKI)

An industrial nanofiltration plant type ET-NF-12000/A (INF1) is installed on BZR premises with permeate production capacity of 12,000 L/h, while industrial nanofiltration plant (INF2), type ET-NF-10000/A, that produces 10,000 L/h of permeate is functioning in BKI. Produced permeate is used as hygienically clean water for drinking, pool filling, and refilling on both locations. Waste water nanofiltration concentrates from both INF1 (NFC1-ZR) and INF2 (NFC2-KI) are discharged into local sewage systems. The goal of NFCP investigations was to explore nanofiltration removal efficiency when exposed to high organic and inorganic containing NF concentrates. Physicochemical composition of investigated NFC1-ZR and NFC1-KI concentrates is shown in **Table 3** with presentation of national maximum acceptable concentrations (MAC). INF1 and INF2 industrial plants have secured enough amount of concentrate for normal PNF operation. Both NFC1-ZR and NFC1-KI were transported

Experiment name	First stage	Second stage	MWCO (Da)
NF90-70-90	NE90 and NE70	NE90	~217
NF3-90	NE90 and NE90	NE90	200
NF3-70	NE70 and NE70	NE70	250

Table 2. Membrane configurations used in the NFWP experimental series.

Parameter	Unit	MAC	NFC1-ZR	NFC1-KI
pH	/	6.8–8.5	8.42	8.64
Electrical conductivity (EC)	μS/cm	1,000	3.380	4.650
Permanganate consumption (COD)	mg/L	8	224.40	43.10
Total organic carbon (TOC)	mg/L	/	60.98	19.50
Ammonium ion, NH ₄ ⁺ -N	mg/L	0.1	1.54	2.70
Arsenic—total	μg/L	10	451.26	45
Sodium, Na ⁺	mg/L	150	652.94	387.80
Bicarbonates, HCO ₃ ⁻	mg/L	/	3621.14	1,171.57

Table 3. Selected physicochemical parameters of nanofiltration concentrates.

to PNF’s buster pump (BP) under the pressure they obtained on INF1 and INF2 and then to NF membrane pilot plant. Part of newly produced concentrate from INF2-NFC2-KI was recirculated to PNF inlet in order to increase recovery and to reduce the amount of waste water. Flow of the recirculated concentrate was kept constant during the experiments. Newly produced concentrate from INF1, NFC2-ZR, in the BZR experiment series, was not recirculated due to the enormous pressure increase.

Investigations were conducted in a way that concentrate flow rates were changed which had an effect on permeate flow rate and consequently permeate flux, thus providing experimental points. Obtained results present average value of three experimental cycle repetitions for every measuring point.

2.3. NFWP experimental series

NFWP experimental series were conducted on the “Envirotech” d.o.o. company premises, located in the city of Kikinda, province Vojvodina, Serbia. This location is equipped with groundwater well “Sterija” drilled in the second aquifer layer on the depth of 52 m. Physicochemical composition of investigated groundwater is presented in **Table 4**.

Well water was distributed to BP under the submersible well pump pressure and subsequently to the NF pilot plant. At the place where well water is inserted into microfilter MF5, a dosing system DP was used for chemical dosage (**Figure 1B**). This was done with the purpose of calcium, magnesium, iron, and manganese ion complexation. Experimental procedure regarding recirculation flow, permeate flux, and pressures was identical to one described in Section 2.2 of this paper for NFWP experiment series.

Citric acid (CA) and Na₄EDTA solutions, both added with dosing speed of 240, 480, and 720 mL/h, were introduced to the inlet well water during the NFWP investigations, and initial CA and Na₄EDTA concentrations, determined on the basis of self-made preliminary experimental data, were 0.4164 mol/L (80 g/L) and 25 mg/L, respectively. Grundfos DDC 6–10 dosing

pump was used for precise dosage regulation and adjustment of solution quantity with accuracy of 1% where desired solution concentration could be monitored via dosing pump LCD display. NFWP experiments were repeated three times for every membrane configuration (Table 2) and every concentration of both complexing chemicals. Obtained results present average value of three experimental cycle repetitions for every measuring point. Names of the experiments in the NFWP series with regard to membrane configurations and CA and Na₄EDTA dosage quantity are presented in Table 5.

2.4. Analytical methods used for selected physicochemical parameter determination

Preliminary physicochemical analysis of groundwater that presented inlet to PNF, as well as permeates and concentrates produced during NFCP and NFWP experiments, was conducted in “Envirotech” laboratory. Selected parameters were determined with the use of standard methods as follows: pH (pH-meter Hanna Instruments HI 98,150), electrical conductivity (conductometer Hanna Instruments HI 9811-5), and ammonium ion and total dissolved iron and manganese (spectrophotometer Hanna C200). Obtained results were used for instantaneous nanofiltration process monitoring.

Selected parameters of inlet water, permeates, and concentrates produced during the experiments were analyzed by accredited body “Institute for work safety,” Novi Sad. Samples were tested for following parameters: pH (WTW InoLab, Germany); electrical conductivity (Crison Instruments Basic 30 conductometer); total arsenic, iron, and manganese (atomic absorption spectrophotometry Shimadzu Japan, type AA-7000 with GFA); TOC (Analytik Jena/Multi N/C 2100 Instrument); ammonia, sodium, calcium, and magnesium (Ion chromatograph, DIONEX, USA, type IC/ICS 3000); and COD and HCO₃⁻ using standard analytical methods [55].

Parameter	Unit	MAC	Well water
pH	/	6.8–8.5	7.39
Electrical conductivity	μS/cm	1,000	780
TOC	mg/L	/	7.22
Ammonium ion, NH ₄ ⁺ -N	mg/L	0.1	3.24
Sodium, Na ⁺	mg/L	150	80.67
Iron, total	mg/L	0.3	1.79
Manganese, Mn ²⁺	μg/L	50	332
Total hardness	°dH	/	19.77
Calcium, Ca ²⁺	mg/L	200	80.08
Magnesium, Mg ²⁺	mg/L	50	37.11

Table 4. Selected physicochemical parameters of groundwater from “Sterija” well in the city of Kikinda.

Experiment name	Membrane configuration	Dosage quantity (mol/h)	Substance
EX3-1	NF90-70-90	/	/
EX3-2	NF90-70-90	0.1	CA
EX3-3	NF90-70-90	0.2	CA
EX3-4	NF90-70-90	0.3	CA
EX3-5	NF90-70-90	0.016	Na4EDTA
EX3-6	NF90-70-90	0.032	Na4EDTA
EX3-7	NF90-70-90	0.047	Na4EDTA
EX3-8	NF3-90	/	/
EX3-9	NF3-90	0.1	CA
EX3-10	NF3-90	0.2	CA
EX3-11	NF3-90	0.3	CA
EX3-12	NF3-90	0.016	Na4EDTA
EX3-13	NF3-90	0.032	Na4EDTA
EX3-14	NF3-90	0.047	Na4EDTA
EX3-15	NF3-70	/	/
EX3-16	NF3-70	0.1	CA
EX3-17	NF3-70	0.2	CA
EX3-18	NF3-70	0.3	CA
EX3-19	NF3-70	0.016	Na4EDTA
EX3-20	NF3-70	0.032	Na4EDTA
EX3-21	NF3-70	0.047	Na4EDTA

Table 5. NFWP experiments with regard to membrane configurations and CA and Na4EDTA dosage quantity.

3. Results and discussion

Hydraulic parameters such as permeate flux and pressures were monitored during the experiments that lead to transmembrane pressure [56] and membrane efficiency [57] calculation.

3.1. NFCP series experimental results

Transmembrane pressure influence on COD, TOC, arsenic, bicarbonate, ammonia, and sodium removal efficiency is presented in **Figure 2**. Removal of easily oxidizable matter expressed via COD was more efficient during EX1 (**Figure 2A**), while total dissolved organic matter showed better removal rate in EX2 experiment. COD and TOC values decreased in average 190 and 57 times, respectively, with regard to inlet water concentration in EX1, and

37 and 18 times, respectively, in EX2. Dissolved organic matter concentration in all the experiments was below MAC [58]. Total organic carbon separation was very efficient in both EX1 and EX2 from 96.74 to 99.10% and 97.88 to 99.70%, respectively. Removal of organic matter expressed via COD was very efficient as well with ξ values of 99.33 to 99.60% in EX1 and 96.49–99.00% in EX2 (**Figure 2A**). The largest portion (> 98%) of dissolved organic matter has MWCO larger than 200 Da, and this is the reason for NOM excellent separation on NF membranes (**Figure 2A**). NOM is removed by NF membranes on two principles, size exclusion and electrostatic repulsion, considering the fact that membranes are in most cases negatively charged [59]. During EX1 investigations arsenic was removed with 98.86–99.38% efficiency, while in EX2 this number was a little lower and valued 94.63–98.75% (**Figure 2A**) where arsenic concentration decreased in average ~115 and ~17 times with regard to inlet concentrations. Obtained total arsenic values were below MAC in all produced permeates [58]. Significantly higher and better arsenic ion retention, with regard to permeate flux, was observed in organic matter-rich environment (EX1). Due to the high organic content, arsenic ions were probably bonded with NOM functional group complex compounds, which could be referred as organoarsenic compounds. These findings of extremely good organoarsenic removal in organic-rich environment confirm previous results [60, 61]. Sodium ion retention was reported with lower efficiency than organic matter and total arsenic in both experiments (**Figure 2B**), with ξ values of 92.25–93.93% in EX1 and 90.44 to 94.51% in EX2. Investigated NF membranes were surrounded with influent that contained dissolved salts where dynamic equilibrium occurred. Concentration of positively charged sodium ions as opposed to negatively charged membrane was greater as long as the concentration of ions of the same charge, like membranes, was less in membrane phase than on the membrane surface. Created Donnan potential prevents equally charged ion diffusion from membrane phase to membrane surface as well as diffusion of oppositely charged ions from membrane surface to membrane phase [62]. Experimentally obtained data for sodium ion rejections can lead to the conclusion that ions were probably rejected from the filtration membrane layer by Donnan effect.

Bicarbonate ions are separated to the concentrate stream with great percentage, in average ~96% in EX1 and ~97% in EX2. Separation of bicarbonate ions on membranes is followed by their decomposition to CO_2 and water via carbonic acid as intermediate compound. Bicarbonate decomposition is generated by electrostatic phenomenon and steric effects under elevated pressure in membrane pores. Complete bicarbonate buffer system is present in NF system. Reaction equilibrium is preferentially shifted to the right side in concentrate phase, where bicarbonate and hydronium ions dominate, while opposite occurs in permeate phase where reaction equilibrium is shifted left where weak carbonic acid and carbon (IV)-oxide and water are present. Ammonium ion separation from water solution was the least efficient of all observed parameters (**Figure 2B**). Ammonium ion was most successfully removed in EX1 with average permeate value of 0.2 mg/L, where this value presents reduction of inlet concentration ~9 times. TMP increase had positive effect on ammonium ion removal with significant increase in removal efficiency. Low ammonium ion removal rate is typical for nanofiltration membranes due to the ammonium MWCO of ~18 Da that is value similar to one that water molecule possesses. At the influent pH > 8.40, most of NOM carboxyl groups are deprotonated, while amino groups, i.e., ammonium ions, are protonated [63]. This phenomenon has an effect

on weak electrostatic attraction occurrence and ammonium ions binding on carboxyl groups which, as a constitutive part of heterogenic humic and fulvic acid solution, are rejected to the concentrate. In this way, small ammonia ions are assimilated into NOM macromolecules with average MWCO values of 500–1500 Da [64], which are building elements of supramolecular structures. Detected ammonium ion concentration in both experiments was above MAC [58], with exception in EX1 where these concentrations were in accordance with EU recommendations for quality of water intended for human consumption [65].

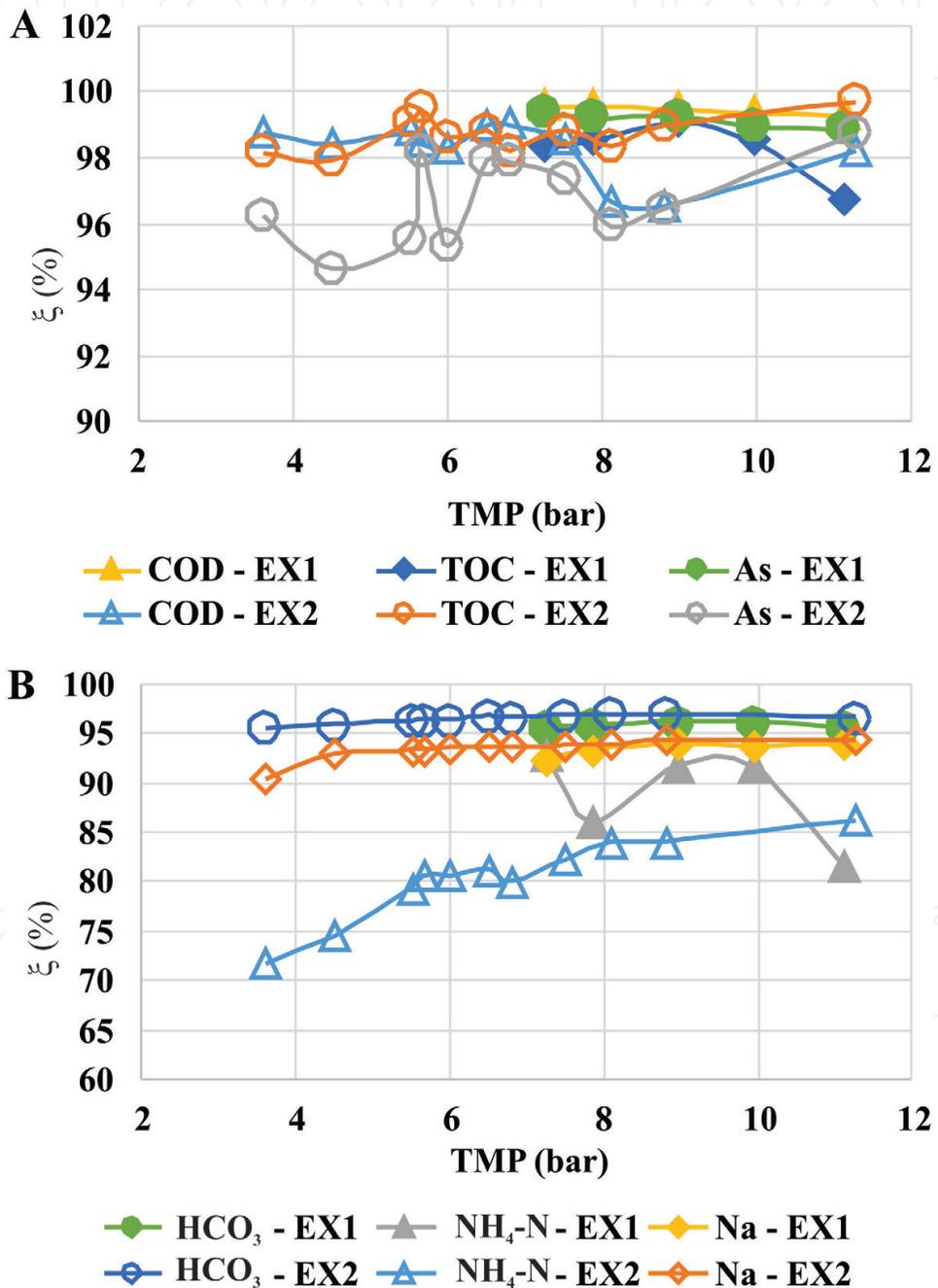


Figure 2. Transmembrane pressure influence on (A) COD, TOC, and total As and (B) bicarbonate ion, ammonium ion, and sodium ion removal efficiency.

3.2. NFWP experimental series results

NFWP experimental series included simultaneous comparison of observed metal ion separation efficiency with regard to applied NF membrane configuration and complexing chemical compound dosing concentrations. Fe_t ion, Mn(II) , Ca(II) , and Mg(II) removal efficiency was calculated and presented in **Figures 3–6** in the dependence of transmembrane pressure. Observed permeability changes of different membranes and their different position arrangement in the system were especially discussed with regard to atomic radius dimension (AR), presented in Å, of investigated metal ion hydrates [66], molecular topological polar surface area (TPSA) in Å² [67], their complexes with CA and Na₄EDTA and maximal projection area (MPA) in Å², of metal ions. Metal ions in aquatic solution are through ion-dipole bonds of mainly electrostatic character bound with water molecules [68]. Certain ion hydration process depends on electrostatic attraction of water molecule and that ion. Considering that attraction of water molecules in the ion environment depends on ion charge density, smaller ions, i.e., ions with larger ionic potential, attract bigger number of water molecules [69]. Radii of hydrated iron, manganese, calcium, and magnesium ions equal 6, 6, 6, and 8 Å, respectively, and MPA of the same ions equals 12.57, 12.57, 15.74, and 15.74 Å², respectively. If organic substances like citric acid or EDTA are added to aquatic solution, substitution of one or more water molecules from hydrated metal ion environment with chelate groups occurs, thus producing coordinative compounds, i.e., complex ions.

Total iron ions are removed with excellent efficiency with 99.77% regardless of applied pressure (**Figure 3A**) in EX-8 experiment without dosage and in EX3-9 to EX3-11 with the dosage of CA solution. NF90-70-90 membrane configuration in EX3-1 and EX3-2 reduces Fe_t concentration from ~85 to ~93%. Addition of larger amounts of CA influences the increase of ξ in EX3-3 and EX3-4 to ~97%. ξ_{Fet} exhibits decrease with TMP increase only in EX3-15 and EX3-18, while simultaneously in EX3-16 and EX3-17 increases to ~5 bar and then decreases again. The lowest removal rate is observed in experiments with NF3-70 membrane configuration. The size of probably created iron and citrate complexes, such as iron (III) citrate ($M_i = 244.94$ g/mol, TPSA = 141 Å²) and iron(II) citrate ($M_i = 245.95$ g/mol, TPSA = 138 Å²), suggests the possibility of steric and electrostatic competitions in molecule transport through the limited space of curvaceous channels in membrane material. This is especially pronounced in NF3-70 configuration in **Figure 3A** where the largest difference in coordinative iron and citrate compound retention was observed. Iron ions are removed with great efficiency (**Figure 3B**), while this percentage is significantly lower in investigations with three NF 4040-70 membranes. Removal efficiency is decreasing with TMP increase in Na₄EDTA dosage experiments where NF3-90 configuration was used. Increase in Na₄EDTA dosage concentration in EX3-5 to EX3-7 influences increase in iron removal efficiency by ~10% in regard to EX3-1. Competition during retention on membranes is also observable, especially in NF3-70 in complexes iron(III)-EDTA ($M_i = 366.98$ g/mol, TPSA = 167 Å²) and iron(II)-EDTA ($M_i = 346.0$ g/mol, TPSA = 167 Å²). The highest Mn(II) removal of average 97.36%, regardless of CA dosage, was done by membranes with MWCO of 200 Da (**Figure 4A**). Manganese ion separation process in other two series is more efficient with the addition of CA complexing agent. Manganese removal efficiency was increased for ~15% with membrane configuration NF90-70-90 with the addition of CA. The lowest Mn²⁺ removal rate of ~70% was observed

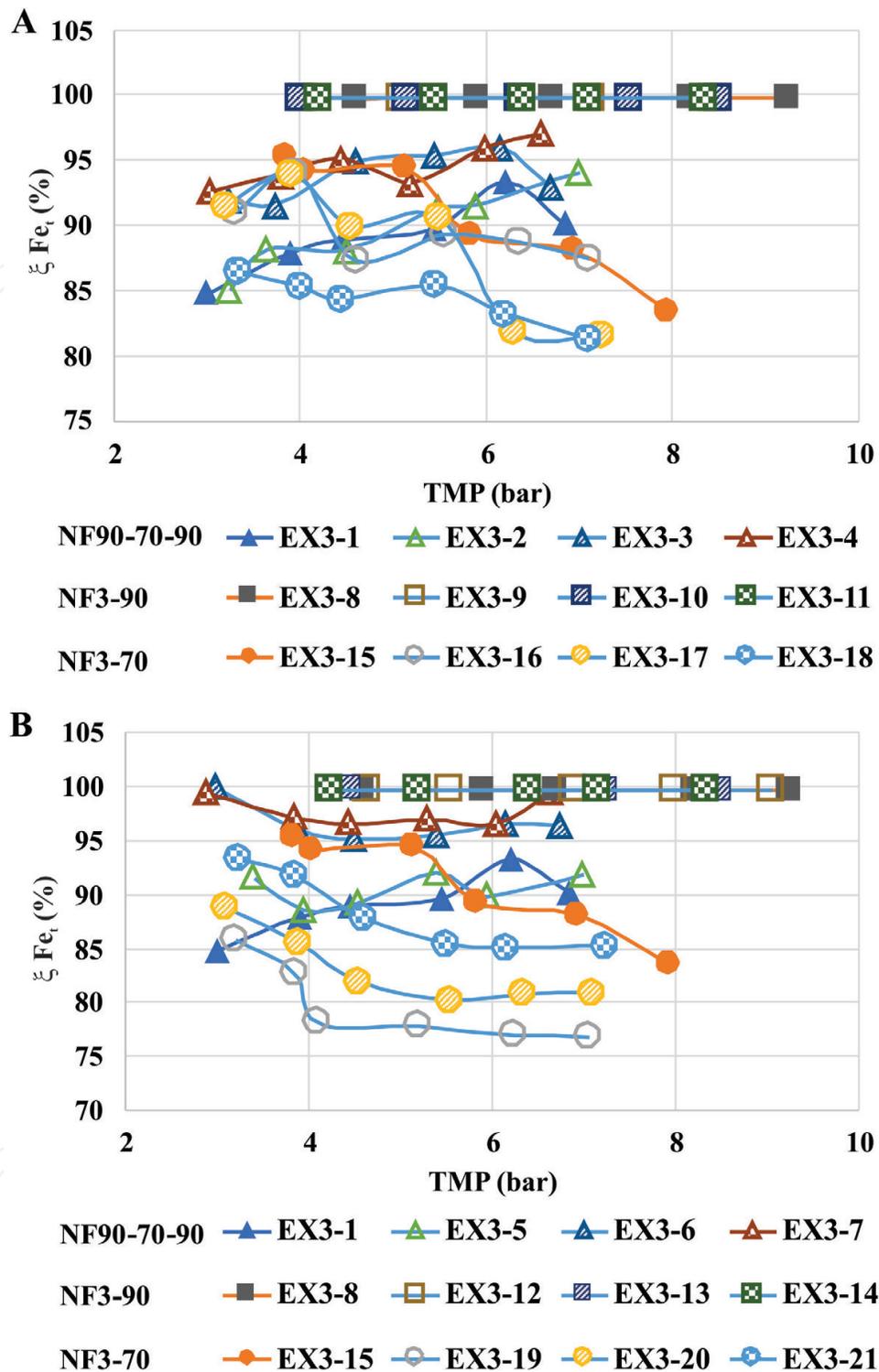


Figure 3. Influence of transmembrane pressure on iron removal from groundwater water (EX3-1, EX3-8, and EX3-15) and from groundwater with addition of CA solution (A) and Na₄EDTA (B) with regard to NF membrane configuration.

in experiments EX-16 to EX3-18. Manganese(II) citrate molar mass ($M_i = 244.94$ g/mol) and TPSA of 138 \AA^2 follow, to a high degree, separation by size with regard to MWCO of investigated membranes (**Figure 4A**).

The best manganese removal with the addition of Na₄EDTA solution was reported in experiments with NF3-90 membrane configuration with average efficiency of 97.36% (Figure 4B). Other two membrane configurations showed excellent ability for $\xi_{Mn(II)}$ increase proportional

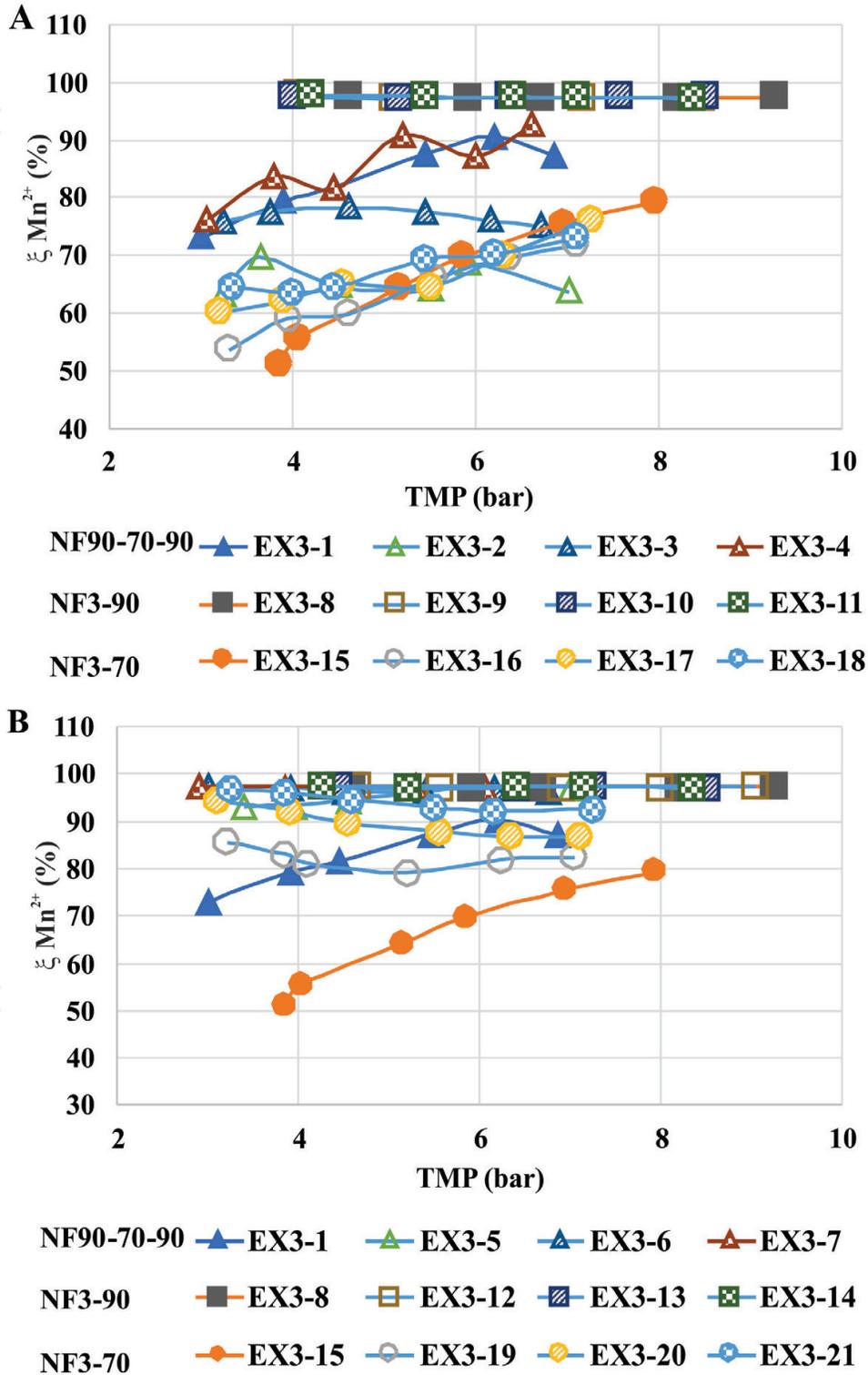


Figure 4. TMP influence on manganese removal from well water (EX3-1, EX3-8, and EX3-15) and well water with addition of CA solution (A) and Na₄EDTA solution (B) in all experimental membrane configurations.

to Na₄EDTA dosage concentration. Average increase in removal efficiency to 85.34% was observed in membrane system with 217 Da MWCO with the highest concentration of chelate agent, while MWCO of 250 Da membrane configuration has, proportionally to Na₄EDTA concentration increase, enabled $\xi_{\text{Mn(II)}}$ increase from 66 to 96.65%. In EDTA, manganese(II) complex ($M_i = 345.01$ g/mol, $\text{TPSA} = 167 \text{ \AA}^2$) retention on the membranes was significantly increased with regard to citrate manganese complexes, even in the membrane configuration with the highest MWCO. This can be contributed to electrostatic forces and Donnan potential difference that obviously were preferential over separation by size.

Fe_i and Mn(II) ions' AR and MPA values are identical, but retention of these ions is significantly altered with addition of complexing ligands into the influent, except in 200 Da MWCO membrane configuration. Increase in TMP values has affected the most $\xi_{\text{Ca(II)}}$ increase in NF3-70 membrane configuration (**Figure 5A**) where this value was increased from ~40 to ~70% in the range of investigated pressures. It is evident that increase in CA dosage influenced removal efficiency value rise to TMP of ~5 bar. Obtained values for removal efficiency were in the range of ~75 to ~90%, where better values were obtained with CA dosage in membrane configuration with MWCO of 217 Da. NF3-90 membranes have removed Ca(II) ions with the highest removal efficiency, regardless of TMP values and CA dosage concentration. Average $\xi_{\text{Ca(II)}}$ for membranes with MWCO of 200 Da equaled 97.26% (**Figure 5A**). Ca(II) ion rejection was 40 to 50% more pronounced than the results observed in previous investigations [70] in experiments with NF90-70-90 and NF3-90 membrane configurations. Dimensions of probably formed tricalcium dicitrate of $M_i = 467.89$ g/mol and $\text{TPSA} = 281 \text{ \AA}^2$ were convenient for separation by size for all three MWCO dimensions. Lower $\xi_{\text{Ca(II)}}$ is evident from EX3-19 to EX3-21 investigations comparing to Ca(II) removal efficiency from well water (**Figure 5B**), while Na₄EDTA dosage did not have any effect on calcium ion retention with NF90-70-90 membrane configuration. Average removal efficiency calculated in NF3-90 experiments with addition of Na₄EDTA was 97.54%. The greatest $\xi_{\text{Ca(II)}}$ value increase with TMP rise was recorded in the NF3-90 investigations and the least in NF3-70 experiments. Even though Ca(II)-EDTA complex is smaller ($M_i = 330.04$ g/mol, $\text{TPSA} = 161 \text{ \AA}^2$) than citrate calcium ion complex, their retention on the membranes is reduced probably due to the electrostatic repulsion, especially in NF3-70 experiments with regard to EX3-15. AR and MPA values for calcium ions are identical to corresponding values for Fe_i and Mn(II) ions. Calcium ion retention is, however, quite different from iron and manganese removal efficiency changes.

CA dosage did not have any significant effect on removal of magnesium ions with regard to removal efficiency with no dosage (experiments EX3-15 to EX3-18). Observed oscillations in ξ values with TMP changes are recorded in experiments with NF90-70-90, especially in EX3-2 where lower values of removal efficiency were calculated with regard to well water filtration with no complexing agent addition. The tightest NF membranes removed magnesium ions with approximately equal ξ , and TMP or CA had negligible effect on these values that were ~95%. Tangential filtration of complex trimagnesium dicitrate molecule ($M_i = 449.96$ g/mol, $\text{TPSA} = 281 \text{ \AA}^2$) with MWCO of 200 and 217 Da affected significant dispersion of retention experimental results in the dependence of CA dosage concentration. Influence of membrane charge and steric effects on the attraction of these complex molecules is evident.

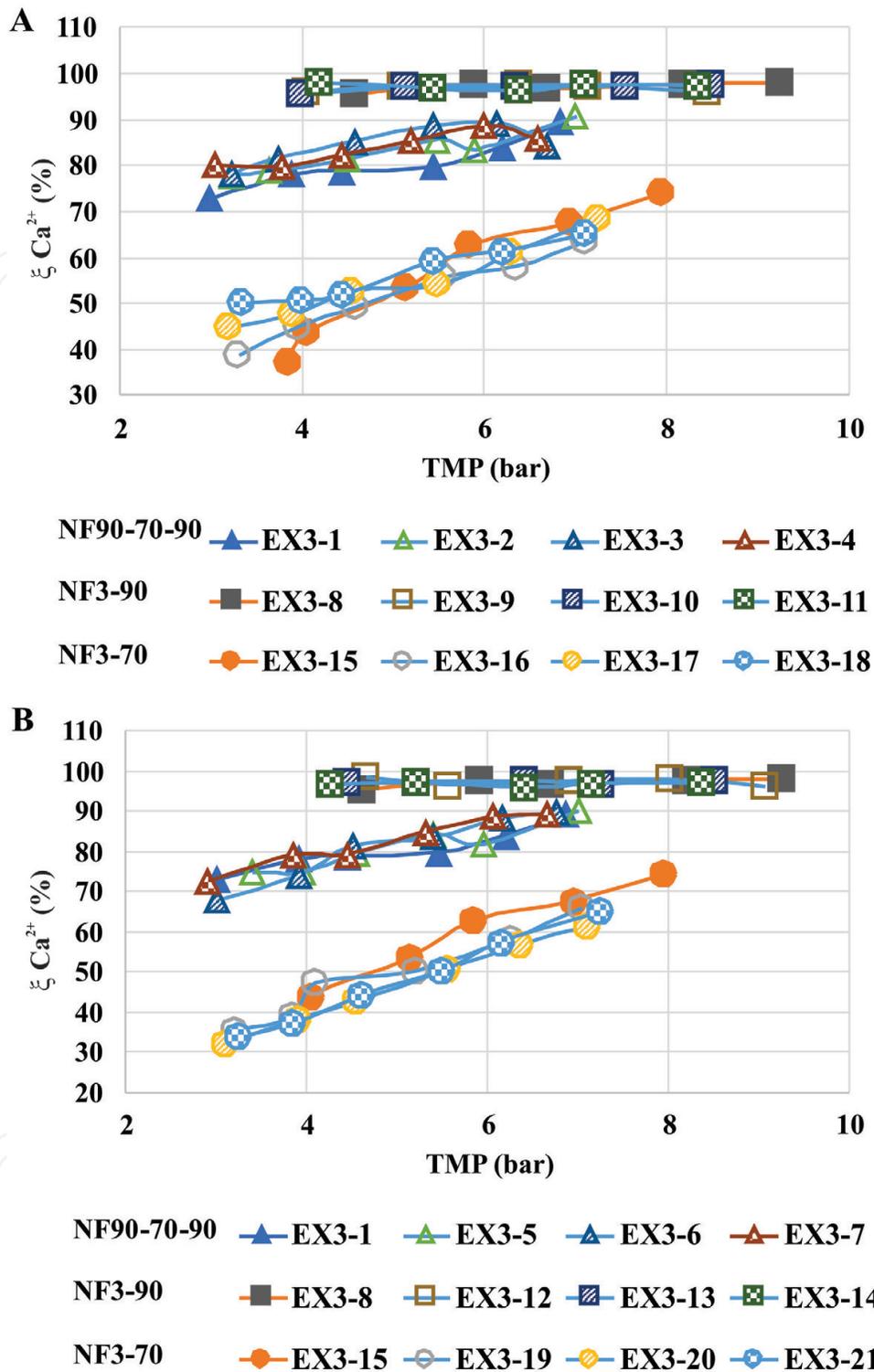


Figure 5. Influence of NF configuration on calcium ion removal efficiency from raw water (EX3-1, EX3-8, and EX3-15) and from raw water with addition of CA solution (A) and Na4EDTA (B) in the dependence of TMP.

Less values of Mg(II) ion removal efficiency were observed in experiments EX3-19 to EX3-21 with Na4EDTA addition with regard to EX3-15 with well water. Similar to results from **Figure 6A**, the highest $\xi_{\text{Mg(II)}}$ values were obtained in the experiments with NF3-90 configuration (**Figure 6B**). With the highest Na4EDTA concentration, magnesium ion removal was the lowest in EX3-7

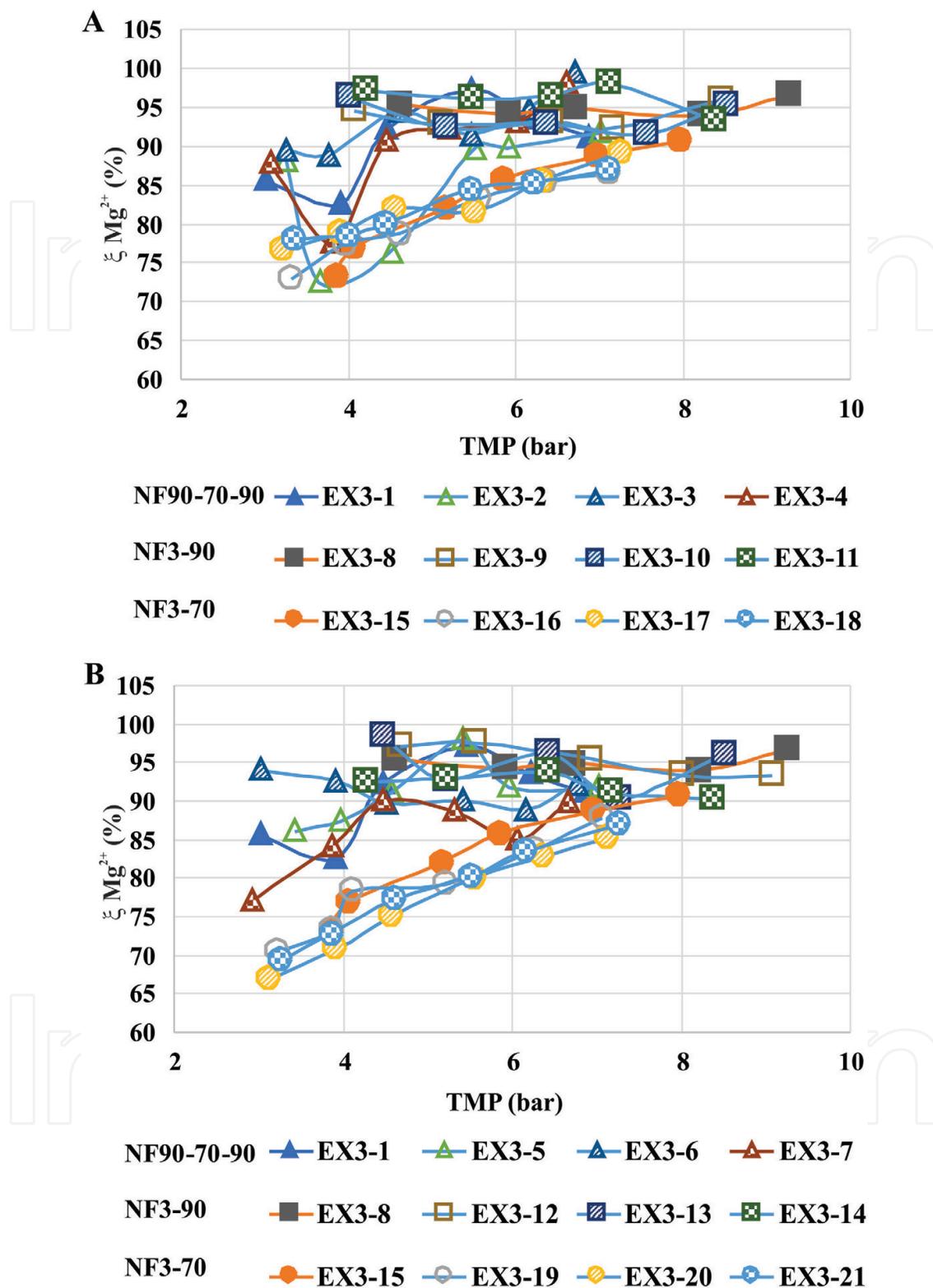


Figure 6. Transmembrane pressure influence on magnesium ξ changes with regard to NF membrane configuration. Experiment with well water: EX3-1, EX3-8, and EX3-15. Experiments with well water + CA solution (A). Experiments with well water + Na₄EDTA (B).

experiments. Magnesium(II)-EDTA complex ($M_i = 358.02 \text{ g/mol}$, $\text{TPSA} = 167 \text{ \AA}^2$) is significantly smaller than magnesium citrate complex ion. Retention results are coherent and almost identical to results obtained in membrane configurations with MWCO of 200 and 217 Da with

regard to Mg(II) citrate complex, where Mg(II)-EDTA complexes are removed with lower efficiency with 250 Da MWCO membranes. Magnesium(II) ion's AR is larger and MPA is equal to one of Ca(II) ions. Mg(II) ion retention is characterized by significant dispersion of $\xi_{\text{Mg(II)}}$ values in the experiments with organic ligand dosage with regard to experiments with well water, except when MF3-70 configuration was used (Figure 6).

4. Conclusions

Semi-industrial investigations of high concentration of dissolved organic matter, total arsenic ions, ammonium ions, $\text{Na}^+_{(\text{aq})}$ and bicarbonate separation presented in NFCP experiment series showed nanofiltration ability for good removal efficiency of stated parameters from waste water. Arsenic ions were chemically bonded with NOM anions into organoarsenic complexes. Applied membranes with 200 Da MWCO removed with greater efficiency higher NOM and total arsenic ion concentrations providing permeates that contained arsenic and NOM in concentrations below maximum tolerable concentrations. It was found that organic matter concentration can be of essence when designing arsenic removal drinking water and waste water plant.

Metal ion separation by different types of nanofiltration membranes and their different configurations with and without addition of citric acid and Na₄EDTA as complexing agent provided several conclusions on membrane behavior. NF3-90 membrane configuration has proved extremely suitable for iron and manganese ion separation regardless of CA and Na₄EDTA solution dosage. Removal of Fe using membrane configuration with higher MWCO (NF90-70-90) showed more intensive separation in addition of complexing agents, while using NF3-70 membrane combination, total iron ion retention was very poor. Probably, coordinative iron and manganese compound separation mechanism to concentrate is a complex one and is not based entirely on size exclusion, but electrostatic forces play a significant role too.

Calcium(II) separation, both with and without organic compound dosage, was very efficient at MWCO of 200 Da and exclusively depends of particle sizes. Retention of magnesium(II) ions shows particle size separation only at MWCO of 250 Da. Significant effect of CA dosage was not recorded, but addition of Na₄EDTA had negative influence on Mg(II) ion separation. Electrostatic effects are dominant in membrane separation of Mg(II) at MWCO of 217 Da.

Obtained results in semi-industrial scale are practically applicable on the large-scale plants for drinking water preparation from deep wells, as well as from shallow aquifers.

Author details

Nikoleta Kukučka Stojanović* and Miroslav Kukučka

*Address all correspondence to: nikol@envirotech.rs

Envirotech d.o.o., Kikinda, Serbia

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