engineering proceedings

MDPI

Proceeding Paper

Solutions for Reducing the Extreme Hardness in Treated Water †

Petra Malíková *, Jitka Chromíková and Silvie Drabinová

Department of Environmental Engineering, Faculty of Mining and Geology, VSB—Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic; jitka.chromikova@vsb.cz (J.C.); silvie.drabinova@vsb.cz (S.D.)

* Correspondence: petra.malikova@vsb.cz

† Presented at the 5th International Conference on Advances in Environmental Engineering, Ostrava, Czech Republic, 26–28 November 2025.

Abstract

A technology aimed at reducing extremely high water hardness in Chotěšov, a village in the Czech Republic, was developed and tested. Three treatment methods were evaluated under laboratory conditions: softening filtration using a cation exchange resin in the Na^+ cycle (resulting in a 72% reduction in hardness); nanofiltration (NF); and reverse osmosis (RO), which reduced hardness by 71% and 96%, respectively. The mixing of the permeate with treated groundwater at a volume ratio of 1:1 resulted in a further reduction in hardness to 41% with NF permeate and to 53% with RO permeate, relative to the original value.

Keywords: groundwater; hardness removal; water softening; drinking water treatment; ion exchange; reverse osmoses; nanofiltration

1. Introduction

Ensuring access to safe and reliable drinking water remains a significant challenge, particularly for rural and small to medium-sized municipalities that lack access to centralised water treatment facilities. In such cases, water is often sourced from local groundwater and treated on-site, requiring the modernisation and optimisation of existing treatment technologies and distribution infrastructure [1–4]. These needs are further compounded by drought conditions, the age of the equipment, and increasingly stringent regulatory requirements [5].

A salient issue is high water hardness, which is attributable to elevated concentrations of calcium and magnesium ions. This can result in the formation of scale in pipes and appliances, reduced cleaning efficiency, and customer dissatisfaction [6–8]. Although not generally regarded as a significant health hazard, hard water has been linked to the development of kidney stones and to potential cardiovascular complications [9–11]. In response to this challenge, a range of strategies have been implemented by various countries, including those with high levels of hardness, such as Japan and India. These strategies have included the implementation of softening measures in specific regions [12,13]. In contrast, other countries, such as the United States, have opted for a different approach, managing the issue through the development of local guidelines and the promotion of consumer-level solutions [14,15].

In the Czech Republic, water softening is rarely implemented, primarily for small-scale sources, and most commonly using ion exchange, with reverse osmosis (RO) being used less frequently [16]. In many countries—such as the Netherlands, Belgium, France, Denmark, Germany, and the United States—centralised softening of hard or moderately

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Academic Editors: Adriana Estokova, Natalia Junakova, Tomas Dvorsky, Vojtech Vaclavik and Magdalena Balintova

Published: 28 November 2025

Citation: Malíková, P.; Chromíková, J.; Drabinová, S. Solutions for Reducing the Extreme Hardness in Treated Water. *Eng. Proc.* **2025**, *116*, 11. https://doi.org/10.3390/engproc2025116011

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hard water is a common practice. This approach better meets consumer needs, including financial considerations, as the societal costs of decentralised softening and increased use of chemical cleaning agents are generally higher than the costs of centralised water softening. In addition to economic benefits, there are also health and environmental reasons for this practice. Centralised softening helps reduce the corrosion of lead and copper pipes, resulting in lower concentrations of lead and copper not only in drinking water but also in treated wastewater discharged into natural water bodies [16]. An overview of individual technologies in terms of their mechanism of action, effectiveness, applicability, operational and maintenance requirements, water consumption, costs, etc., is provided by Tang et al. (2019) [17] and Tang et al. (2021) [18].

Additionally, there is a mounting interest in the assessment of the trade-offs of softening techniques through life cycle assessment. This involves the balancing of improved appliance lifespan and consumer comfort against the environmental burden of different technologies [19,20].

The present study investigates the applicability of three softening technologies—namely, cation exchange, nanofiltration (NF), and reverse osmosis (RO)—under laboratory conditions. The objective of this study is to evaluate the efficacy of these processes in reducing the levels of extreme water hardness in groundwater from the Chotěšov drinking water treatment plant (DWTP) in the Czech Republic. Furthermore, the study will assess their potential for integration into existing treatment processes.

2. Materials and Methods

2.1. Groundwater Characteristics

Experiments were conducted using real groundwater samples from the Chotěšov drinking water treatment plant (DWTP), which uses a groundwater source. The plant produces around 90,000 m^3 of drinking water per year and supplies approximately 3000 people. Its operation is based on water demand and reservoir level. The current treatment process involves aerating the raw water using a horizontal aerator, filtering it through two pressure filters filled with granular manganese oxide and dosing it with sodium hypochlorite, potassium permanganate and sodium hydroxide for disinfection and stabilisation. The treated water is then stored in a reservoir and distributed through the water supply network.

2.2. Experimental Set-Up

To optimise the existing treatment technology at the DWTP, three methods were tested at laboratory scale: a softening filtration, nanofiltration (NF), and reverse osmosis (RO). The feed water used in the experiments was treated groundwater from the DWTP accumulation tank, without the addition of disinfection or stabilisation reagents.

2.2.1. Softening Filtration

For the experiments, a strongly acidic cation exchange resin in the Na^+ cycle—Purolite C100E supplied by Ecolab Purolite s.r.o. (Ústí nad Labem, Czech Republic) (hereafter referred to as 'resin')—was selected. Its basic characteristics are summarised in Table S1. A 3.2 cm diameter glass column, fitted with a frit and a control valve, was filled with 7.6 g of activated resin (volume 10 mL). According to the manufacturer's instructions, the resin was preconditioned for six hours in a 10% NaCl solution prior to use. Treated groundwater from the DWTP was passed through the column. After each 0.5 L sample had been processed, the eluate was analysed for pH, electrical conductivity (EC), neutralisation capacity (acidity and alkalinity) and Ca^{2+} and Mg^{2+} concentrations. The equations used to calculate the hydraulic loading rate and flow velocity were:

$$h = V \cdot V_0 \cdot t \ (L/L \cdot h), \quad (1)$$

where h is the hydraulic loading rate, V is the sample volume passed through the column in litres, V_0 is the volume of the resin in litres, and t is the time in hours.

$$v = V \cdot P \cdot t \text{ (m/h)} \quad (2)$$

where v is the flow velocity, V is the sample volume passed through the column in m^3, P is the cross-sectional area of the column in m^2, and t is the time in hours.

After the resin had been exhausted, it was regenerated using a 10% NaCl solution, and the concentrations of Ca^{2+} and Mg^{2+} were determined. The regenerated resin was then rinsed with demineralised water and 1 litre of DWTP groundwater was passed through the column again. The same parameters were monitored in the eluate.

2.2.2. Membrane Filtration

To assess the suitability of pressure membrane filtration, laboratory-scale batch tests were conducted using the MMS SW18 unit (MMS AG Membrane Systems, Urdorf, Switzerland). A commercial spiral-wound membrane (1812-TS40-31) was used for nanofiltration (NF), and another (1812-ACM2-31) for reverse osmosis (RO), both supplied by MICRODYN-NADIR, a MANN+HUMMEL company (Wiesbaden, Germany). The characteristics and operational parameters of both membranes are summarised in Table S2. Salt solution tests were performed using a 0.5% magnesium sulphate solution for NF and a 0.5% sodium chloride solution for RO.

Each experimental cross-flow filtration run followed this sequence: an initial salt test with the model solution; three consecutive tests with treated groundwater from the DWTP; and a final salt test to evaluate potential membrane fouling. Operating pressures were set at 4, 6, 8, and 10 bar for NF, and at 10, 15, and 20 bar for RO. Membrane filtration was performed in a mode with retentate recycling. In each test, 5 litres of either the salt solution or DWTP water were processed. The volume ratio of permeate to retentate was set to 2.55 L:2.45 L. Once the target permeate volume was reached, the test was terminated.

The following parameters were recorded automatically: feed pressure, permeate pressure, pressure drop (Δp), temperature of the feed solution, permeate flow rate, flux, volume concentration ratio (VCR), and time. Permeate and retentate samples from the first DWTP water test were collected for detailed analysis. The remaining permeates from both NF and RO were mixed 1:1 with DWTP water. All samples—including feeds, permeates, retentates, and the mixed samples—were analysed for the following indicators: pH, electrical conductivity (EC), neutralisation capacities (acidity and alkalinity), total dissolved solids (TDS): pH, EC, neutralisation capacities (acidity, alkalinity), TDS, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$.

2.3. Analytical Methods

The pH, EC and temperature were measured using WTW 340i multiparameter instruments (Xylem Analytics Germany Sales GmbH & Co. KG, WTW, Weilheim, Germany). Time was tracked using a laboratory timer and standard laboratory equipment and glassware were used throughout the experiments. Relevant water quality parameters, including neutralisation capacities, major ions and TDS, were determined using standard analytical methods. All chemicals used to prepare model solutions and regeneration agents were of analytical grade.

3. Results and Discussion

3.1. Groundwater Characteristics

The results of the long-term monitoring of treated groundwater that has undergone the DWTP process are summarised in Table S3. The results demonstrate that the DWTP

consistently produces high-quality drinking water over the long term. The only negative factor is the elevated Ca^{2+} and Mg^{2+} content, which leads to very high carbonate-calcium hardness of the water. The average Ca^{2+} concentration is 125 mg/L, whereas the recommended value according to Czech legislation is 40–80 mg/L. Conversely, the Mg^{2+} content of the treated water aligns with the recommended Czech legislative values of 20–30 mg/L; the average measured concentration is 27 mg/L. The total hardness of the water, a specifically monitored parameter, reaches an average value of 4.22 mmol/L (ΣCa + Mg) and 425.08 mg/L ($CaCO_3$), which is approximately 0.7 mmol/L higher than the limit recommended by Czech legislation. Consequently, consumers exert pressure on the operator or supplier of drinking water.

3.2. Softening Filtration

During the laboratory experiments, the cation exchange resin required flushing to capacity with 4.5 L of water from the DWTP. Table 1 shows the values of the monitored parameters in the eluates, as well as the recorded time taken for the samples to pass through the column, including the calculated values: hydraulic column load and flow rate. As can be seen, the monitored values in the eluate after cation exchange resin regeneration are similar to those in eluate samples 2 and 3.

Table 1. Groundwater characteristics during softening with ion exchange resin PUROLITE C100E.

Sample	Time h	Treated Volume L	pH -	EC µS/cm	Acidity mmol/L	Alkal. mmol/L	ΣCa + Mg mmol/L	Ca mg/L	Mg mg/L	$CaCO_3$ mg/L	h L/L·h	v m/s
input	0.00	0.0	7.99	949	4.11	0.33	4.65	121.72	39.31	465.81	-	-
1	0.21	0.5	7.93	983	3.91	0.21	1.45	34.34	14.42	145.13	238.10	2.96
2	0.22	1.0	8.18	1010	4.12	0.22	1.34	31.70	13.31	133.97	227.27	2.83
3	0.24	1.5	8.20	1011	4.11	0.14	1.32	28.86	14.66	132.43	208.33	2.59
4	0.24	2.0	8.22	1008	4.12	0.18	1.52	34.54	15.90	151.72	208.33	2.59
5	0.24	2.5	8.18	996	4.07	0.18	1.92	47.75	17.74	192.29	208.33	2.59
6	0.24	3.0	8.17	980	4.12	0.19	2.91	83.31	20.21	291.25	208.33	2.59
7	0.24	3.5	8.15	970	4.14	0.26	3.84	111.76	25.51	384.11	208.33	2.59
8	0.24	4.0	8.00	960	4.11	0.31	4.06	117.86	27.11	405.94	208.33	2.59
9	0.24	4.5	7.94	950	4.12	0.24	4.33	121.72	31.42	433.32	208.33	2.59
After ion exchanger regeneration												
10	0.46	1.0	8.06	950	4.12	0.24	1.31	32.72	11.95	130.91	217.39	2.70

If the existing DWTP technology were supplemented with softening filtration using cation exchange resin in the Na^+ cycle, it would meet the recommended values for Ca^{2+} and Mg^{2+} indicators. This would ensure that the recommended values for Ca^{2+} and Mg^{2+} are met. At the same time, the treated water would be classified as medium hard, which is an improvement of two hardness classes (72% reduction). The outcomes of the present study are commensurate with the results reported by Tang et al. (2021) [18].

3.3. Membrane Filtration

A total of seven series of pressure membrane filtration tests were performed in the laboratory using water from the DWTP. A summary of the individual tests is provided in Table S4, including average flux values and the time taken to produce 2.55 L of permeate. There were negligible differences between salt tests with $MgSO_4$ and NaCl before and after treatment with DWTP water, indicating no membrane fouling effect during either NF or RO. Clearly, as operating pressure increases, the test duration decreases. Generally, achieving higher permeate flux is desirable because it improves process performance [18]. It can be concluded that the membranes used were satisfactory.

The quality of the permeate and retentate samples is presented in Tables 2, 3, S5 and S6. The quality of the mixed permeate, obtained by blending the permeate with untreated

DWTP water, is shown in Table 4. The rejection of the selected indicators is further elaborated upon in Table S7. In the event of the value of the rejection coefficient for a given component being equal to 1, it can be deduced that this component does not pass through the membrane and is completely retained. With regard to hardness, untreated DWTP water is classified as very hard (4.98 mmol/L ΣCa + Mg). The present findings indicate that the efficacy of NF and RO is comparable to that reported in Tang et al. (2021) [18]. The reduction in the hardness of groundwater was found to be 71% in the case of NF, and 96% in the case of RO.

Table 2. Water quality parameters before and after NF of groundwater at the DWTP.

Sample	Pressure Bar	pH -	EC µS/cm	Acidity mmol/L	Alkal. mmol/L	∑Ca + Mg mmol/L	Ca mg/L	Mg mg/L	$CaCO_3$ mg/L	SO_4^{2-} mg/L	HCO_3^- mg/L	TDS mg/L
feed		7.56	951	4.08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	4	7.45	396	1.61	0.18	1.45	44.49	8.26	145.11	0.01	10.98	0.26
retentate		7.70	1317	5.38	0.56	6.26	197.59	32.33	626.52	250.00	34.16	1.14
feed		7.56	951	4.08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	6	7.34	350	1.39	0.20	1.46	44.09	8.75	146.13	0.01	12.20	0.23
retentate		7.94	1402	6.09	0.42	7.23	212.42	46.91	723.59	300.00	25.62	1.19
feed		7.56	951	4.08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	8	7.32	329	1.17	0.17	1.47	32.87	15.80	147.14	2.00	10.37	0.21
retentate		7.93	1421	6.23	0.36	7.85	225.25	54.20	785.64	245.00	21.96	1.23
feed		7.56	951	4.08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	10	7.38	307	1.12	0.18	1.35	32.06	13.37	135.11	1.00	10.98	0.19
retentate		7.94	1480	6.57	0.58	7.79	233.27	47.88	779.65	255.00	35.38	1.28

Table 3. Water quality parameters before and after RO of groundwater at the DWTP.

Sample	Pressure Bar	pH -	EC µS/cm	Acidity mmol/L	Alkal. mmol/L	∑Ca + Mg mmol/L	Ca mg/L	Mg mg/L	$CaCO_3$ mg/L	SO_4^{2-} mg/L	HCO_3^- mg/L	TDS mg/L
feed		7.56	951	4.08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	10	7.45	11	0.09	0.15	0.15	0.01	3.65	15.06	3.00	9.15	0.01
retentate		7.76	1655	6.95	0.92	7.50	222.98	47.08	750.66	300.00	56.12	1.36
feed		7.56	951	4,08	0.51	4.98	137.47	37.67	498.39	104.00	31.11	0.76
permeate	15	7.23	13	0.10	0.27	0.14	0.01	3.40	14.03	3.00	16.47	0.02
retentate		7.72	1666	6.98	0.83	7.97	243.29	46.18	797.66	315.00	50.63	1.40
feed		7.05	937	4.14	1.18	4.58	132.10	31.16	458.17	180.00	72.16	0.73
permeate	20	7.71	15	0.09	0.21	0.18	0.01	4.26	17.57	2.00	12.96	0.05
retentate		7.86	1709	7.56	1.41	6.92	210.16	40.70	692.37	300.00	86.24	1.35

Table 4. Water quality parameters of RO and NF permeates mixed 1:1 with groundwater at the DWTP.

Sample	pH -	EC µS/cm	Acidity mmol/L	Alkal. mmol/L	∑Ca + Mg mmol/L	Ca mg/L	Mg mg/L	$CaCO_3$ mg/L	SO_4^{2-} mg/L	HCO_3^- mg/L	TDS mg/L
NF permeate: groundwater	7.81	643.00	2.61	0.50	2.94	90.63	16.51	294.29	54.00	30.44	0.47
RO permeate: groundwater	7.74	487.00	1.85	0.35	2.32	34.14	35.74	232.42	55.50	21.42	0.37

The mixing of NF permeate with untreated DWTP water at a ratio of 1:1 has been demonstrated to reduce the hardness level to that of hard water (softening by 2.4 mmol/L of total hardness, with an efficiency of 41%). In a similar manner, the mixing of RO permeate with untreated DWTP water at an equal ratio results in moderately hard water (softening by 2.66 mmol/L of ΣCa + Mg, with a 53% efficiency of total hardness).

4. Conclusions

Supplementing the existing technology at the Chotěšov DWTP with a softening unit based on ion exchange would lead to increased operational costs. This would mainly

be due to higher electricity consumption, the need for regeneration chemicals (e.g., resin replacement), modifications to the control system and increased water usage. Sodium chloride in tablet form would be used as the regenerant, with an estimated consumption of 0.7 kg per m^3 of produced water. Given the plant's average annual production of 90,000 m^3, the additional chemical costs would be around CZK 25,000. Electricity consumption would increase by around 4 kWh, resulting in an additional 1600 kWh per month, with annual energy costs rising by over CZK 100,000.

Alternatively, supplementing the current system with a reverse osmosis (RO) membrane filtration unit, including a cleaning and flushing system, antiscalant dosing, sodium metabisulphite for chlorine removal, a flow metre and a mixing system to combine softened and unsoftened water at a ratio of 1:1, would also increase operating costs. These would include higher water and electricity usage, system integration costs and membrane replacement costs. Electricity consumption would increase by around 6 kWh, equating to 2300 kWh per month, resulting in a total annual increase in operating costs of over CZK 150,000. However, if the technology were upgraded to include a nanofiltration (NF) membrane unit, the permeate could potentially meet drinking water quality requirements.

Accordingly, the issues of water hardness, ageing infrastructure, and the need for effective local treatment solutions are critical in policy discussions. Importantly, the interplay between consumer expectations and regulatory requirements will continue to shape the landscape of drinking water treatment, making it essential for communities to develop tailored, context-specific solutions that prioritise both health outcomes and environmental sustainability.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/engproc2025116011/s1, Table S1: Purolite C100E characteristics; Table S2: Membrane characteristics and operating parameters; Table S3: Water quality of groundwater treated by the existing treatment process (without softening); Table S4: Summary of NF and RO tests; Table S5: Monitored parameters in the feed and effluent streams during NF of 0.5% $MgSO_4$ saline solution; Table S6: Monitored parameters in the feed and effluent streams during RO of 0.5% NaCl saline solution; Table S7: Rejection factor of selected parameters in NF and RO.

Author Contributions: P.M., J.C. and S.D. have been involved in all aspects of the manuscript such as conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original preparation, writing—review and editing, visualisation, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sets are contained within the article. Further data and materials requests should be addressed to the corresponding author.

Acknowledgments: The authors would like to thank the Department of Environmental Engineering, Faculty of Mining and Geology for technical and material support connected with laboratory analyses.

Conflicts of Interest: The authors declare no conflict of interest.

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