GROUNDWATER TREATMENT BY MEMBRANE TECHNOLOGIES FOR HOUSEHOLD PURPOSES

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Abstract: *The aim of the presented article is to design membrane water treatment technology for Spiš area in Slovakia in such a way that the treated water from a well fulfils the quality criteria of water for household purposes. Particular objectives include an analysis of water in the studied well, determination of the concentration of selected indicators of drinking water quality and their comparison with the limit values given in the legislation of the Slovak Republic concerning the quality of water intended for human consumption. The first step was to determine the values of following indicators: pH, conductivity, temperature, TDS, dissolved chlorides, sulphates, calcium, magnesium,* COD_{Mn}*, phosphates, nitrates, ammonium ions and selected heavy metals. The water from the well was subsequently treated by selected membrane processes (1st stage - microfiltration, 2nd stage - reverse osmosis) and after each stage the analysis of the above mentioned parameters was performed again. In the final part, the results are presented: in the original water sample from the well, the limit values of drinking water quality indicators were not exceeded; after adjustment by microfiltration the set values of the indicators were lower than in the original sample. The second stage of reverse osmosis treatment resulted in demineralised water, which had to undergo an additional degree of treatment in the system which produced remineralised water. Consequently, it can be concluded that the quality of the water has improved in terms of the hardness and presence of nitrates, and it has thus been confirmed that the membrane technologies performed are an effective way of treating drinking water.*

Key words: *groundwater, microfiltration, reverse osmosis, indicators*

1 INTRODUCTION

Groundwater is water under the ground. Collected in saturated zones it is important for engineering work, geological studies, drinking water sources and irrigation. Groundwater is relatively free of pollution and is therefore very important for domestic and small industrial use. In arid areas, groundwater is the only source of domestic consumption and irrigation. A large part of the precipitation and water from rivers and lakes are connected to groundwater by means of infiltration and subsequent percolation [1].

Slovakia has good hydrological and hydrogeological conditions for the formation, circulation and accumulation of groundwater, yet the great disadvantage is its uneven distribution. The smallest quantity of groundwater is located in Prešov and Nitra Regions and vice versa, Bratislava and Trnava Regions record the most significant quantities of groundwater [2].

The sources and reserves of groundwater in Slovakia vary depending on the location, time and quality. Although these waters are renewed, that does not mean that they are unlimited, and only by their optimal use they can ensure their relative inexhaustibility [3].

2 THE STUDY AREA

According to the regional geomorphological division of Slovakia, the given area – surroundings of the well – is included in the Fatra-Tatra Region, in Hornádská kotlina Basin and Hornádske podolie Sub-valley. Hornádska kotlina Basin has an upland to low-mountain relief character. The fragmentation is conditional to geological structure; The altitude of the area is 470 m above sea level [4].

The surroundings of the well belong to the Hornád River Basin, which runs about 70 m to the south. Hornád River is included in the list of watermarked watercourses and is classified as a water supply course from the 136.7 to 168.9 river km. Groundwater in Spišská Nová Ves area and its surroundings is characterized by shallow horizon of underground waters of the quaternary fluvial sediments. The groundwater level changes over the year, depending on climate change, even 1 m [4].

3 MEMBRANE TECHNOLOGY

Groundwater treatment using membranes is common for many applications, including softening, desalination, TDS reduction and removal of specific components such as iron or arsenic [5]. Water is supplied to the membrane device. The water is divided into two streams by the membrane [6]:

- permeate that passes through the membrane and is free of pollution, and
- retentate (concentrate) containing entrapped substances.

Thin, semi-permeable films (membranes) are used in membrane processes, which can be characterized as selective permeable barriers. They represent a physical barrier that catches substances without their temperature, chemical or biological change [6].

Microfiltration is closest to conventional filtration in terms of membrane processes. Separation occurs on the basis of particle size (0.1 to 10 μm) captured on the membrane. The applied microfiltration pressure is relatively low compared to other filtration processes (<0.2 MPa). It is often used as a pre-treatment of water for subsequent treatment by reverse osmosis or electro dialysis. It is a reliable barrier method for removing solid micro-particles, micro-organisms and other pollutants from water from various sources (particles, viruses, bacteria). Due to its fine porosity, the membrane ensures a high and constant quality of water flow [7].

Reverse osmosis is a high pressure method used to remove dissolved metals and salts from water. Because of the typical pore size and high separation ability, reverse osmosis is an effective way to remove almost all conventional water contaminants except volatile organic compounds [5]. It works on the same principle as microfiltration, ultrafiltration and nanofiltration, it differs with used membranes and applied pressure. It removes particles with a size of 0.1-1 nm [6]. Reverse osmosis is characterized by removing all excess substances from water, causing demineralisation of water. This demineralized water is disposed of significant minerals that are irreplaceable to the organism. However, according to hygienists, long-term drinking of such treated water can cause serious illnesses (bone degeneration, cardiovascular disease, nail fracture, etc.). Reverse osmosis water treatment is therefore recommended to be used when the only available water source is water with higher mineralization or water containing hazardous solutes. In the process, it is necessary to maintain a certain mineralization so that the quality corresponds to the requirements for potable water. Therefore, it is advisable to ensure remineralization of water (e.g. mixing with untreated treated water, filtration through natural materials, etc.) [8].

4 METHODS

The procedures of determining the selected indicators in the water sample from the well in Spišská Nová Ves are as follows:

- determination of concentrations of calcium, magnesium, chloride, sulphate and chemical oxygen demand (COD_{Mn}) by chemical laboratory analysis,
- determination of concentrations of ammonium, phosphate and nitrate by photometry (Palintest, USA),
- determination of pH, temperature and water conductivity of Hanna Combo multimetre,
- determination of heavy metal concentrations by atomic adsorption spectrophotometry (iCE 3300 Thermo Scientific, USA).

The water analysis was performed in the original untreated water and subsequently after the selected membrane processes.

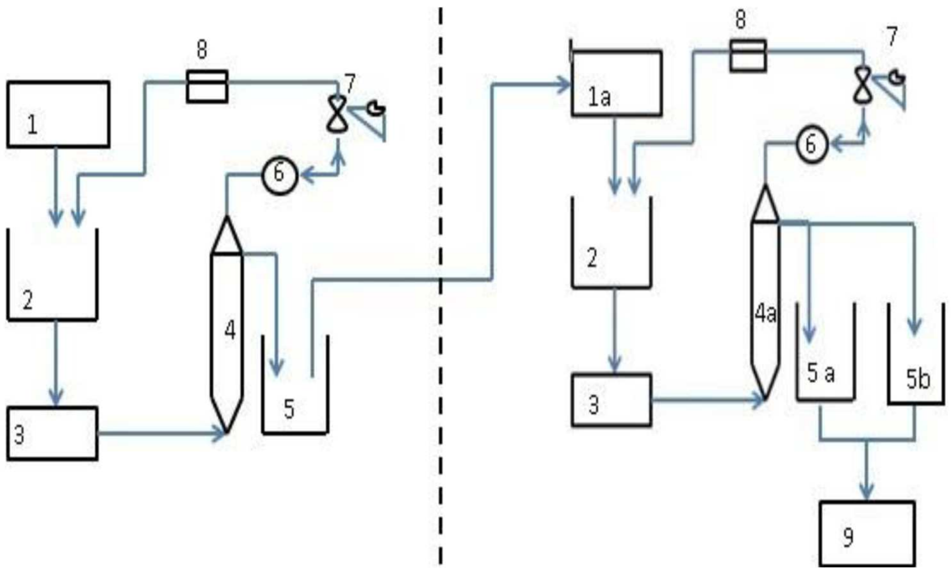

Fig. 1 Process of water treatment

Key: 1 – analysis of original sample before treatment, 1a – analysis of water after microfiltration, 2 – water input, 3 – pump, 4 – microfiltration membrane, 4a – osmotic membrane, 5 – permeate, 5a – remineralised water, 5b – demineralised water, 6 – pressure sensor, 7 – valve, 8 – induction flow meter, 9 – water analysis after treatment

Water analysis was performed in the original untreated state; water was then treated by selected membrane processes (1st stage - microfiltration and 2nd stage - reverse osmosis). After each stage of treatment, the analysis of the above mentioned parameters was performed again. It is necessary to add that after microfiltration the output was one permeate, part of the permeate was taken to determine the concentration of selected indicators and the remaining part was subsequently treated in the second stage of treatment - reverse osmosis. The output of the reverse osmosis treatment was (1) remineralised and (2) demineralized water and the final concentrations of the above mentioned parameters were measured (Fig. 1).

Microfiltration system is equipped with a ceramic membrane. The effective membrane layer is made of α-Al_2O_3, which is attached to a solid porous supporting layer. The membrane is resistant to mechanical stress, pressure shock, and heat up to 150°C. The pH range is from 0.5 to 13.5, which allows the membrane to be cleaned with harsh chemicals. The membrane has a tubular form whose internal diameter is 7 mm and length 25 cm. The average membrane pore size is 0.1 - 0.5 μm [9].

The reverse osmosis system operates on 5-stage filtration. In the first stage, undesirable staining, unpleasant odor, and fine sediments are removed from the water. In the second stage, a filter with a lined activated charcoal filter which dechlorinates the water is used. Further, chlorination by-products are removed from water by the next filter and, in particular, it functions as a protection of osmotic membrane which is particularly sensitive to chlorine. Possible damage to the membrane by activated carbon fragments is prevented by the third stage of treatment. The fourth stage is a specific osmotic semi-permeable membrane. The fifth stage, through which the purified water flows, eliminates residual impurities such as dioxins and free gases.

Since the treated water is demineralized, an additional stage is included behind the whole reverse osmosis system, which enriches the demineralised water with minerals, especially, but not only, calcium and magnesium. In this system, it is a particular mineralizer called Semidol [10]. Semidol is dolomitic filtering material approved by DIN EN 1017 and DIN 2000 for the treatment of drinking water, pool water, industrial water, and also for de-acidification and removal of iron, manganese and silicates. The pure $CaCO_3.MgO$ content is greater than 99%. Semidol is therefore very well suited as a filter material. It is white because it is pure, and its grains are homogeneous, porous with a rough surface without cracks [10].

5 RESULTS

This part of the paper presents the results obtained from measurements of the individual indicators of drinking water quality in the studied sample in four different states (namely before and after each treatment by membrane technologies).

Calcium is one of the indicators necessary in drinking water. The limit value in the government regulation [12] is > 30 $mg.l^{-1}$. As it can be seen from the graph (Fig. 2), the original sample of water before treatment contained 134.27 $mg.l^{-1}$ of calcium. After adjustment, these values were reduced to a final concentration of 32.06 $mg.l^{-1}$.

As it can be seen from the graph (Fig. 3), magnesium concentrations before and after water treatment did not exceed the limit values set by the government regulation [12].

Chlorides belong to the group of harmful substances. Therefore, their values are recorded in the monitoring systems. The government regulation [12] sets the limit value 250 $mg.l^{-1}$. From the graph (Fig. 4) it can be stated that no sample exceeded the limit value.

The limit value [12] for sulfates is 250 $mg.l^{-1}$. Based on the graph (Fig. 5) it can be stated that sulfates before and after the treatment meet the limit value.

Nitrates are chemical compounds that are formed by the combination of nitrogen and oxygen, and are therefore commonly found in water in small amounts. However, nitrate sources are also agricultural fertilizers whose continuous use greatly affects water quality. Under the government regulation [12], the limit is 50 $mg.l^{-1}$ for adults, but 10 $mg.l^{-1}$ for infants. As it can be seen from the graph (Fig. 6), the sample of water before or after treatment has not exceeded the limit value for adults and also for infants.

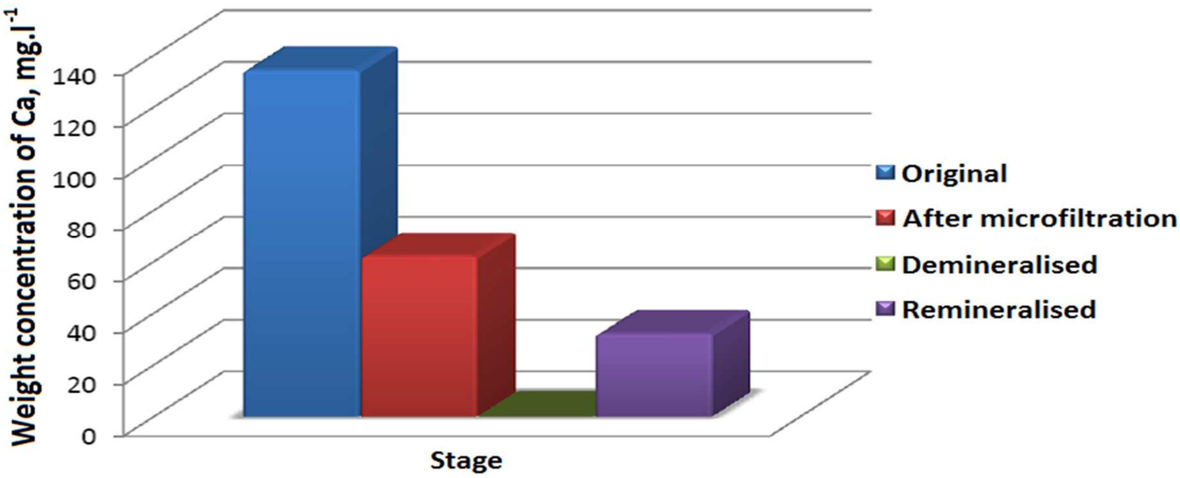

Fig. 2 Calcium concentration after each stage.

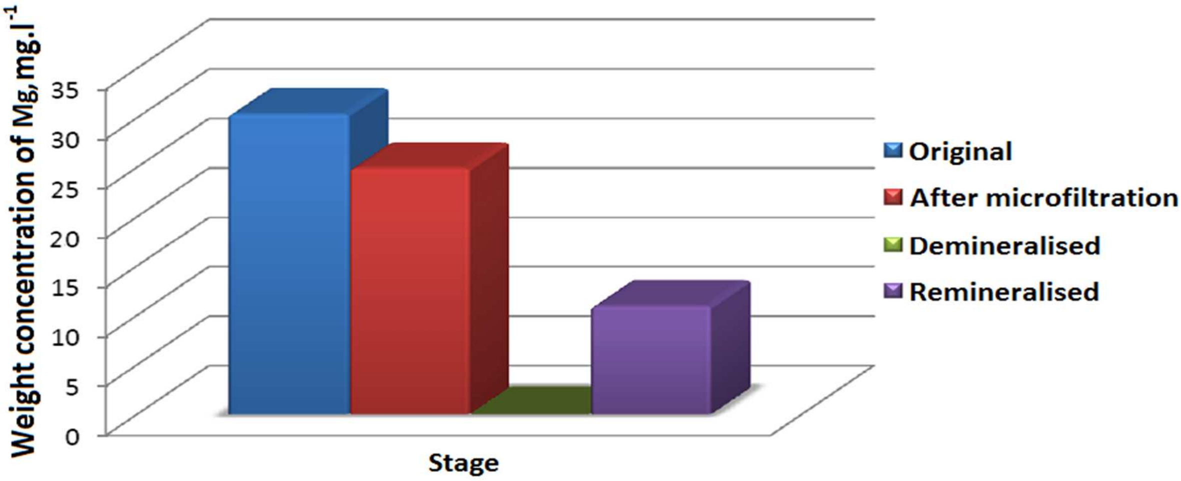

Fig. 3 Magnesium concentration after each stage.

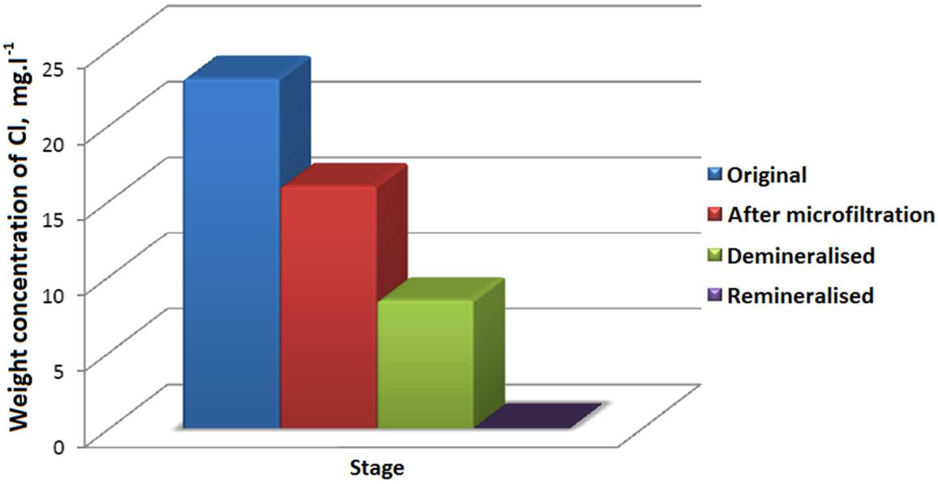

Fig. 4 Chloride concentration after each stage.

However, it should be noted that the concentration of nitrates in the original untreated sample can be increased because there is a household in the surroundings of the well which is not connected to the public sewer. This household is using a “temporary septic tank” through which water passes to the soil.

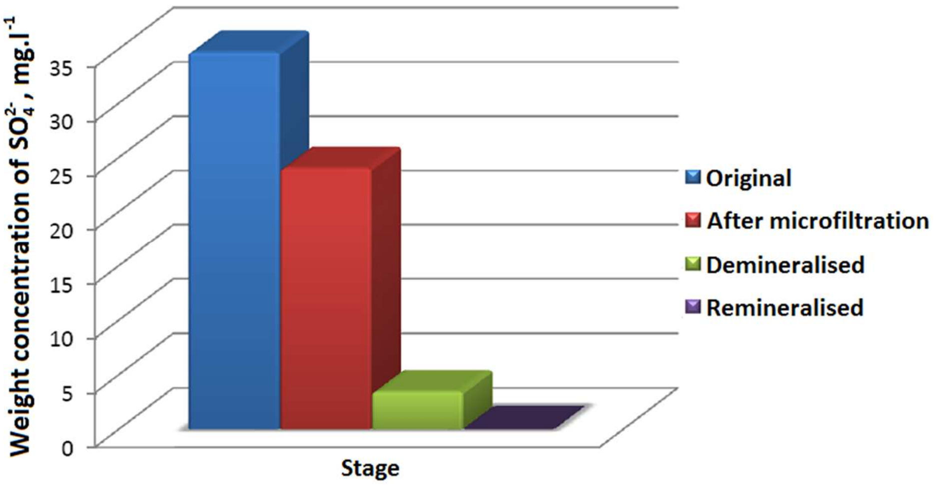

Fig. 5 Sulfate concentration after each stage.

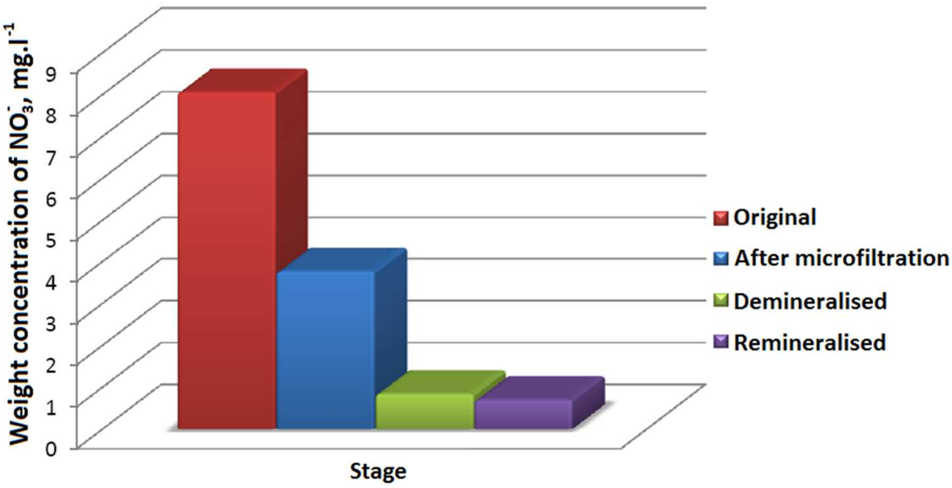

Fig. 6 Nitrate concentration after each stage.

Indicators phosphate and ammonium ions in the original sample were not detected (the photometer measured the values below the detection limit, which is 0 mg.l^{-1} for PO_4^{3-}, and 0 mg.l^{-1} for NH_4^+).

The following table (Table 1) shows changes in the pH, temperature and conductivity of water before and after the treatment by the membrane technologies. According to the government regulation [12] these three indicators are included into a group of indicators that may adversely affect the sensory quality of drinking water. From the measured data it can be assumed that all three indicators meet the limit values according to the legislative standard.

Tab. 1 Change in the values before and after the treatment

Sample	pH	conductivity [mS.m^{-1}]	temperature [°C]
original	7.18	693	10.5
after microfiltration	6.40	756	20.5
demineralised	7.59	0	19.7
remineralised	8.72	104	19.7

6 CONCLUSION

The aim of this work was to design and test water treatment process for water from a well in Spišská Nová Ves using membrane technologies so that the treated water from the well fulfils the qualitative criteria of drinking water.

The water was treated by selected membrane processes (1st stage - microfiltration, 2nd stage - reverse osmosis) and after each individual treatment by membrane filtration the analysis of selected indicators was performed. No limit values for drinking water quality indicators have been exceeded in the original sample water from the well. After adjustment by microfiltration, the set values of the indicators were lower than in the original sample. The final second degree of reverse osmosis treatment resulted in demineralised water, which had to undergo an additional degree of treatment in a system that returned calcium, magnesium and other minerals to get remineralised water.

It would be advisable to continue to determine the presence of microbiological indicators, thereby completing the research of the water in this important aspect. However, it should be noted that even if bacteria or viruses were present in the water, the reverse osmosis treatment would remove them.

Consequently, it can be concluded that the quality of the water has been improved in terms of the hardness and presence of nitrates, and it has thus been confirmed that the membrane technologies performed are an effective way of treating drinking water.

REFERENCES

[1] Das, M.H, Saikia, M.D.: Hydrology. PHI Learning, New Delhi, 2009, pp. 270–281.
[2] VÚVH: Vodné hospodárstvo v Slovenskej republike v roku 2011 [online]. MŽP SR, Bratislava, 2012 [2013-02-12]. Available on-line at: http://www.vuvh.sk/download/dok/ms_2011.pdf.
[3] Patschová, A.: Hodnotenie zdrojov podzemných vôd SR a ich využívania. Podzemná voda VIII, 2002, pp. 13-23.
[4] Hujo, P.: Obchodné centrum SC Tulip Spišská Nová Ves. Zámer podľa Národnej rady Slovenskej republiky č. 24/2006 Z. z. o posudzovaní vplyvov na životné prostredie [on-line]. Žilina, 2008. [cit. 2013-02-01]. Available on-line at: http://www.enviroportal.sk/sk/eia/detail/obchodne-centrum-sc-tulip-spisska-nova-ves.
[5] Odel, L.H.: Treatment Technologies for Groundwater. American Water Works Association, Denver 2010, pp. 56-60.
[6] Bindzar, J. et al.: Základy úpravy a čištění vod. VŠCHT, Praha, 2009.
[7] Wang, L.K, Chen, J.P., Hung, Y., Shammas, N.K.: Membrane and Desalination Technologies. Springer (Humana Press), New York, 2011, p. 485.
[8] Kriš, J., Galík, M.: Kedy je potrebná úprava vody v domácnostiach. Voda Zlín 2012: XVI. mezinárodní vodohospodářská conference, Zlín (ČR), 15.-16.3.2012. 2012, pp. 85–90.

[9] Búziková, Ž.: Mikrofiltrácia kvasničnej biomasy cez keramické membrány. Diploma thesis. Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava. 1997.
[10] Semidol [on-line]. Dolomitwerk [cit. 2013-03-20]. Available on-line at: http://www.dolomitwerk.de/en/list-of-material/semidol/.