The analysis of chemical parameters of groundwater before and after sand filtration in the Velekinca water treatment plant, Kosovo

Valdrin M. BELULI

University of Mitrovica “Isa Boletini”, Faculty of Food Technology, Department of Technology, Str. Ukshin Kovaçica, 40000 Mitrovica, Republic of Kosovo

University of Tirana, Faculty of Nature Sciences, Department of Industrial Chemistry, Str. Boulevard Zogu I, 1001 Tirana, Albania


Abstract

Our scientific research is based on the monitoring of ions before and after filtration of groundwaters in the water plant of Velekinca in the municipality of Gjilan, Kosovo. Sandy filters are the most commonly used industrial filters in surface – and groundwater industries. The reason is their low construction cost and high processing capacity. In our scientific research, sand filters used in the plant do not have perfect filtration, so we can monitor results before filtration (BF) and after filtration (AF) by determining the concentration of some ions and molecules. The following average concentrations have described: Ca\(^{2+}\) (BF: 83.42, AF: 83.19) mg·dm\(^{-3}\), Mg\(^{2+}\) (BF: 35.59, AF: 34.35) mg·dm\(^{-3}\), Cl\(^{-}\) (BF: 28.018, AF: 28.73) mg·dm\(^{-3}\), SO\(_4^{2-}\) (BF: 42.76, AF: 44.46) mg·dm\(^{-3}\), HCO\(_3^{-}\) (BF: 410.9, AF: 404.81) mg·dm\(^{-3}\), A-HCl (BF: 6.73, AF: 6.63) ml-HCl, GH (BF: 19.94, AF: 19.62) °dH, CS (BF: 18.87, AF: 18.5) °dH and NO\(_2^{-}\) (BF: 0.0033, AF: 0.0022) mg·dm\(^{-3}\). Being scientific researchers in the field of water treatment technology, we have concluded that ions create an affinity for sand particles. They attach to each other by creating an ion-sand particle physical chain. According to our scientific research, sand filters are difficult to guarantee a high quality of water processing.

Key words: groundwater treatment plant, ion-sand particle chain, physical-chemical parameters, sand filtration, WHO standard

INTRODUCTION

Water diversion is a globally historic and popular engineering method for water supply [Dai et al. 2018]. Water security is of paramount concern, particularly in countries facing significant population growth and a drying climate [Bekele et al. 2018]. The analysis of water produced is critical to monitor field operation, control processes, evaluate appropriate management practices and treatment effectiveness, and assess potential risks to public health and environment during the use of treated water [Jiang et al. 2021]. Groundwater chemistry provides enormous vital information on suitability for domestic, irrigational and industrial purposes, and it is very helpful in understanding and identifying processes determining the hydrochemical quality of groundwater [Alam 2014; Xiao et al. 2017]. Rare earth elements concentrations in groundwater vary depending on specific water-rock interactions and the presence of dissolved or colloidal organic and inorganic species, etc. [Dai et al. 2000; Liu et al. 2018]. Since high concentrations of ions signal certain problems, water to be clean should be physically and chemically processed.

When transferred from laboratories to industrial applications, processes need to be more durable in operation and production. This has been accomplished by a growing number of operators in the industry who carefully followed and collected process data. The cost of the process, ever larger capacity of plants, and difficult working conditions have forced the creation of a new engineering discipline, which today is called a galopant development. In order to generate a normal performance of industrial processes, a set of measurements and adjustments need to be per-
formed on working chemical or physical parameters [PIN-
GULI et al. 2017]. Our research is based in the field of en-
vironmental science, i.e. quality of groundwater in the
groundwater treatment plant (GWTP). Sand filters have
been our main focus because they accumulate different
chemical ions that can cause problems in water processed
directly for consumption.
Both calcium and magnesium are essential to human
health. Inadequate intake of either nutrient can impair
health [COTRUVO, BARTRAM (eds.) 2009]. The presence of
the soluble Ca$^{2+}$ and Mg$^{2+}$ salts causes unsuitable behav-
ior of hard water solutions for drinking, watering, and
industrial purposes [CETIN 2014; VIERO et al. 2002]. Hard
water is usually defined as water which contains a high
concentration of calcium and magnesium ions. Carbonate
hardness is sometimes called temporary hardness because
it can be removed by boiling. Non-carbonate hardness
(carbon strength) cannot be broken down by boiling of
water, so it is also known as permanent hardness etc. [BE-
LULI 2017].
Chlorides are the most widespread anions in surface
and groundwater, and the concentration of chlorides in
natural waters varies. Chlorides are not considered very
desirable, but in most cases its concentration from 70–150
mg·dm$^{-3}$ causes serious problems for humans and plants
[DACI, DACI-AJVAZI 2014]. Sulphate ions, as well as chlor-
ide ions, are found in all-natural waters. In groundwater,
SO$_4$ content is generally higher than in rivers and lakes.
The main source of sulphate ions in water is gypsum [SHEHU
2009]. The main source of nitrite ions (NO$_2$-N) in water is
the process of mineralization of organic matter and nitrifi-
cation from bacteria [BELULI 2019]. Nitrite is the ionic
intermediate state between nitrate and ammonia nitrogen,
which explains their low quantities encountered in the aquat-
ic environment [KADAOUI et al. 2019]. However, studies
on acute and chronic effects of nitrite in various parts of
the world have shown that their different concentrations in
water and nutrients lead to several diseases in different
population groups [PARVIZISHAD et al. 2017]. Ground-
water can traverse the surface layers of soil until it reaches
water accumulation areas, which are indescribable rock
layers. Often, these are limestone formations but also gyp-
sum, clayey, etc. Water that has been in contact with lime-
stone layers is enriched with HCO$_3$ [BELULI et al. 2017].

After that, we have analysed chemical parameters such as
calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), chlorides (Cl$^-$),
general hardness (GH:°dH), carbon strength (CS:°dH), alkal-
ine (A:HCl), bicarbonate (HCO$_3$), and nitrite (NO$_2$-N).

These chemical parameters have been analysed in the
groundwater analytic laboratory and are compared with
data provided by the World Health Organization (WHO),
see Table 1.

**STUDY METHODS**

**SAMPLING IN THE GROUNDWATER TREATMENT
PLANT (GWTP)**

Sampling techniques are relatively important in analyt-
icism, especially when samples do not have so
much suspended solids (e.g. drinking water samples). The
volume of samples is good to be 0.5–2.0 dm$^3$ [ÇULLAJ
2010]. Water samples in our scientific research have been
determined in the laboratory of analytical and instrumental
chemistry, so the samples are not transported outside the
industry because all scientific research is based inside the
industrial facility and the discussion of results and exper-
imental part is discussed and monitored by experts for wa-
ter technology (Figs. 1, 2).

### Table 1. Permissibility criteria for physical-chemical parameters according to WHO

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Measurement unit</th>
<th>WHO standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>Ca$^{2+}$</td>
<td>mg·dm$^{-3}$</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg$^{2+}$</td>
<td>mg·dm$^{-3}$</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Cl$^-$</td>
<td>mg·dm$^{-3}$</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Nitrites</td>
<td>NO$_2$-N</td>
<td>mg·dm$^{-3}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>HCO$_3$</td>
<td>mg·dm$^{-3}$</td>
<td>630</td>
</tr>
<tr>
<td>Alkaline</td>
<td>A:HCl</td>
<td>cm$^{-1}$</td>
<td>10.5</td>
</tr>
<tr>
<td>General hardness</td>
<td>GH:°dH</td>
<td>–</td>
<td>30</td>
</tr>
<tr>
<td>Sulphate</td>
<td>SO$_4$-</td>
<td>mg·dm$^{-3}$</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>

Source: WHO [1972].

**SAND BED FILTER DESIGN IN THE WATER
TREATMENT PLANT IN VELEKINCA**

Regardless of the application, the recommended depth
of the sand is around 0.6–1.8 m [COULSON et al. 1991]. The
sand bed depth in the two water treatment plants is 1.5 m.
Dimensions of the sand filters are as follows: width 2 m and length 4 m (Photo 1). A compromise is that most rapid pressure sand bed filters use sand grains of 0.6–1.2 mm.

The effective diameter (De) and the uniformity coefficient (Cu) are two important granulometric characteristics of a filter material. The coefficient of uniformity is the ratio between the diameter that allows the passage of 60% of particles and the one that allows the passage of 10%; the proportion D60:D10. The main elements of these filters include the end of the filter, gravel support and the filter medium. The end of the filter is a structure that separates the filter medium from filtered water. It is stable and it holds the filter medium (1 m sand and gravel) and the water that is above the filter medium. It also allows to collect and remove filter water and uniform distribution of washing water [OSMANAJ, LAKO 2017], see Figure 3.

The gravel support is place on the bottom of the filter. It keeps the sand of the filter medium and regulates the distribution of washing water in the filter. The filter medium contains very fine sand of 0.4–1.0 mm in diameter.

CHEMICALS

Ethylenediaminetetraacetic acid (EDTA), Nitri Ver 3 reagent (HACH®), Sulfa Ver 4 (HACH®), AgNO3 (C = 0.01 mol·dm−3), HCl (C = 0.01 mol·dm−3), buffer, indicator (black erythromycin), indicator (methylorange), indicator (phenolphthalein), indicator (black murexide), NaOH (C = 2 mol·dm−3), methylene chloride, K2Cr2O7, H2SO4 98%, glucose.

CHEMICAL PARAMETERS AND METHODS OF ANALYSIS

Absorption spectrometry is based on the electromagnetic radiation absorption by molecules in the UV spectra of 160–400 nm (ultraviolet) and VIS 400–780 nm (visible). UV-VIS radiation absorption causes the excitation of electrons in chemical bonds by pushing molecules to higher energy levels [VASJARI et al. 2013]. The absorption of UV-VIS radiation from complex molecules and inorganic salts of transitional metals, as well as of lanthanides and actinides, causes the molecule to move from its basal to its excited state [BELULI 2018]. The HACH® Model DR/2010 Spectrophotometer is a microprocessor-controlled single-beam instrument for colorimetric testing in the laboratory or in the field [Hach 1999]. The instrument is precalibrated for over 120 different colorimetric measurements and allows convenient calibrations for user-entered and future HACH methods.

Sulphate (SO42−) concentration has been determined using Sulfa Ver 4 (0–70 mg·dm−3), method 8051), and the absorbance level is then measured using a spectrophotometer (HACH® DR/4000) at λ = 450 nm. Nitrite (NO2-N) concentration is determined using Nitri Ver 3 reagent (test 0–0.300 mg·dm−3, method 8507), and the absorbance level measured using a spectrophotometer (HACH® DR/2010) at λ = 507 nm.

Water hardness or general hardness (GH) is analysed by adding 2–5 cm3 of buffer and indicator (black erythromycin) in very small quantities to a sample of 100 cm3 of water. Following the addition of the indicator, the solution becomes red or light red, and the titration is done with complexon III or EDTA (CEDTA = 0.01 mol·dm−3) until the solution changes its colour to intensive blue [BELULI 2018]. The calculation is based on Equation (1):

\[
GH (^{°}dH) = \frac{VE_{\text{EDTA}} \cdot C_{\text{EDTA}} \cdot 56 \cdot 1000}{V_s} \quad (1)
\]

Where: \( V_{\text{EDTA}} \) = the titration volume (cm3) with ethylenediaminetetraacetic acid, \( C_{\text{EDTA}} = 0.01 \text{ mol·dm}^{-3} \), \( V_s \) = the volume of the sample used.

Carbonate strength (CS) is defined as the alkalinity to methylorange. A volume of 100 cm3 water sample was transferred to 500 cm3 Erlenmeyer flask and 2–3 drops of methylene chloride were added. The titration was performed with standard solution HCl (C = 0.01 mol·dm−3)
of water to neutralize acids. Four drops of phenolphthalein are added to 100 cm³ of the sample. If the 100 cm³ solution becomes purple, the pH of water contained bases increases after water filtration. The concentration of Ca²⁺ after filtration varies from 0.74 to 4.32 mg·dm⁻³ (Fig. 4); in SP5, SP6, SP7, SP8, SP9, SP12, SP16, SP17, SP18 and SP19, the concentration of Mg²⁺ is reduced from 0.04 to 3.4 mg·dm⁻³ (Fig. 4).

Results for alkalinity (A-HCl). Alkalinity refers to the capability of water to neutralize acid. A-HCl as a chemical parameter in this research displays no risk and at all times the alkaline concentration is from 6.1 to 7.2 cm³ and it is in compliance with the WHO (Fig. 4, Tab. 1). A-HCl concentrations before and after the filtration of groundwater has changed and we have divided them into two groups based on their concentrations:
a) in samples SP1, SP3, SP6, SP10, SP13, SP14, SP15 and SP20, the concentration of Ca²⁺ in water after filtration is more vivid and varies from 0.98 to 7.2 mg·dm⁻³ (Fig. 4);
b) in the samples SP2, SP4, SP5, SP7, SP8, SP9, SP11, SP12, SP16, SP17, SP18 and SP19, Ca²⁺ concentration after filtration varies from 0.8 to 3.61 mg·dm⁻³ (Fig. 4).

Lab results show that in the first group of calcium samples it has not been reduced after filtration but the concentration of calcium is more present. Increasing the concentration of Ca²⁺ in water after the filter does not pose any risk because the concentration is still in accordance with the WHO regulation (Tab. 1). In the second group of samples, the concentration of Ca²⁺ is reduced but not much.

Results for magnesium (Mg²⁺). In our research, the magnesium concentration (Mg²⁺) as mg·dm⁻³ is not very high and is in line with the WHO (Tab. 1, Fig. 4). The concentration of Mg²⁺ in the GWPT after analysing a large number of water samples before filtration is from 30.5 to 41.7 mg·dm⁻³ (Fig. 4). The concentration of Mg²⁺ after filtration is from 28.3 to 40.1 mg·dm⁻³, specifically in our research in the GWPT after water filtration, different concentrations of Mg²⁺ result from changes after filtering and we have divided them into two groups:
a) in SP1, SP3, SP5, SP11, SP14, SP16, SP18, SP19 and SP20, the concentration of Mg²⁺ has not been reduced, so the concentration of Mg²⁺ increased after filtration from 1.08 to 4.32 mg·dm⁻³ (Fig. 4);
b) in SP2, SP4, SP6, SP7, SP8, SP12, SP13, SP15, SP17 and SP19, the concentration of Mg²⁺ is reduced from 0.04 to 3.4 mg·dm⁻³ (Fig. 4).

RESULTS AND DISCUSSION

Results for calcium (Ca²⁺). The Ca²⁺ ion in groundwater varies from 76.55 to 90.58 mg·dm⁻³ (Fig. 4). The problem exists in water filtration where Ca²⁺ concentration increases after water filtration. The concentration of Ca²⁺ before and after the filtration of groundwater has changed and we have divided them into two groups based on their concentrations:
a) in samples SP1, SP3, SP6, SP10, SP13, SP14, SP15 and SP20, the concentration of Ca²⁺ in water after filtration is more vivid and varies from 0.98 to 7.2 mg·dm⁻³ (Fig. 4);
b) in the samples SP2, SP4, SP5, SP7, SP8, SP9, SP11, SP12, SP16 and SP11, GH after filtration decreases and varies from 0.39 to 0.73 °dH (Fig. 4).
Fig. 4. Results of chemical parameters before and after water filtration in groundwater treatment plant: calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), chlorides (Cl\(^-\)), sulphates (SO\(_4^{2-}\)), bicarbonates (HCO\(_3^-\)), alkalinity (A-HCl), general hardness (GH – °dH), carbonic strength (CS – °dH) and nitrite (NO\(_2^-\)); source: own study
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**Results for carbon strength (CS).** The carbon strength (CS/°dH) means a permanent hardness of water. In our research, CS is from 17.1 to 20.4 °dH (Fig. 4). CS values before and after the filtration of groundwater have changed and we have divided them into two groups:

a) in the SP5, SP6, SP10 and SP11 samples, CS values after filtration increase and vary from 0.3 to 0.6 °dH (Fig. 4);

b) in the SP1, SP2, SP3, SP4, SP7, SP8 and SP9 samples, CS values after filtration decrease and vary from 0 to 0.73 °dH (Fig. 4).

**Results for bicarbonates (HCO_3^-).** In our scientific research, the concentration of HCO_3^- is from 372 to 439 mg·dm⁻³ (Fig. 4). The concentration of HCO_3^- before and after the filtration of groundwater has changed and we have divided its values them into two groups:

a) in samples SP5, SP6, SP9, SP10 and SP11, the HCO_3^- concentration increases and varies from 6.1 to 12 mg·dm⁻³ (Fig. 4);

b) in samples SP1, SP2, SP3, SP4, SP7 and SP8, the concentration of HCO_3^- decreases and varies from 6.1 to 42 mg·dm⁻³ (Fig. 4).

**Results for sulphates (SO_4^{2-}).** Sulphates as a chemical parameter in our scientific research has been determined because sulphates are often present in many groundwaters. The concentration of SO_4^{2-} is from 39.04 to 46.2 mg·dm⁻³ in the groundwater treatment plant (GWPT). Concentration values are in accordance with WHO (Tab. 1, Fig. 4). The samples in the GWPT before and after filtration are divided into two groups:

a) in samples SP1, SP3, SP4, SP5, SP6, SP7 and SP9, the concentration of SO_4^{2-} after filtration increases and varies from 0.4 to 5.12 mg·dm⁻³ (Fig. 4);

b) in samples SP2, SP8, SP10 and SP11, the concentration of SO_4^{2-} decreases and varies from 0.18 to 3.0 mg·dm⁻³ (Fig. 4).

**Results for nitrites (NO_2^-).** Nitrite (NO_2^-) as a chemical parameter is necessary for analysis in surface and groundwaters. Its high concentration displays major problems as explained above. The amount of NO_2^- in our research is from 0.0025 to 0.004 mg·dm⁻³ (Fig. 4). In samples from the GWPT before and after filtration, the NO_2^- concentration is in accordance with the WHO (Tab. 1, Fig. 4). The NO_2^- reduction after filtration is from 0 to 0.002 mg·dm⁻³. After filtration, the concentration of NO_2^- has not increased in comparison to some other chemicals.

**Results for chlorides (Cl^-).** Chlorides before and after filtration are determined to compare the concentration of chloride ion reduction. In our case, the concentration of Cl^- is from 25 to 30.01 mg·dm⁻³ and it is in accordance with the WHO regulation (Fig. 4, Tab. 1). Cl^- concentration values before and after the filtration of groundwater have changed and we have divided them into two groups:

a) in samples SP2, SP6 and SP8, the concentration of Cl^- after filtration increases and varies from 0.4 to 3.0 mg·dm⁻³ (Fig. 4);

b) in the SP1, SP3, SP4, SP5, SP7, SP9, SP10 and SP11 samples, the concentration of Cl^- decreases and varies from 1.0 to 2.5 mg·dm⁻³ (Fig. 4).

Being scientific researchers in the field of water treatment technology, we have concluded that ions create an affinity for sand particles and they attach to each other by creating an ion-sand particles and a physical chain. This is caused by not cleaning the filters often or not cleaning the sand filters well. When water flows into the filter at a certain speed that depends on the daily processing capacity, the water flow captures ions that remain in the filter and increases the concentration of ions after filtration (Fig. 5).

**CONCLUSIONS**

Our scientific research expresses a problem with sand filters that do not guarantee water filtration quality. According to this study, sand filters cannot guarantee a high quality of water processing, as it was the case in the groundwater treatment plant (GWPT). We have examined the question of which ions are the least reduced during the filtration of groundwater. According to the study, the reduction in sand filters of Ca²⁺ and Mg²⁺ ions was insufficient. Therefore, we conclude that when the water flow is larger ions do not stay long in a filter as opposed to a slow-
er flow of water when the concentration of ions inside the sand filter increases after filtration:
- the concentration of Ca$^{2+}$ after water filtration increased from 1 to 7 mg·dm$^{-3}$;
- the concentration of Mg$^{2+}$ after water filtration increased from 1 to 4 mg·dm$^{-3}$;
- the concentration of HCO$_3^-$ after filtration in water increased from 6 to 12 mg·dm$^{-3}$;
- the concentration of SO$_4^{2-}$ after filtration in water increased from 0.4 to 5 mg·dm$^{-3}$;
- the concentration of Cl$^-$ after filtration in water increased from 0.4 to 3 mg·dm$^{-3}$.

The concentration of A-HCl, GH, CS is not taken into account because its pre- and after filtration differences are too low. The second conclusion refers to another scientific study. Sand filters are cleaned approximately every 200 hours of operation. We suggest sand filters to be cleaned after 150 hours because when the filter works nearly 160 hours, the concentration of ions starts to increase gradually. The results of this analytical study have enabled us to understand that the time interval for cleaning sand filters with air is very important because, as shown by analytical results before and after filtration, there is an insufficient reduction of ions. The study helps us to increase the quality of water treatment but it has also been a scientific factor for many water industries in Kosovo.

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