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Araştırma Makalesi / Research Paper

Oxidation of Manganese with Active Use of Potassium Permanganate in the Water Treatment Plants in the Town of Gjilan, Republic of Kosovo

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ABSTRACT

Gjilan (42°27’48’’N 21°28’09.7’’E) is one of the seven biggest cities in the Republic of Kosovo. Water supply for this city is enough for reasons of functioning of two plants of water processing in the city of Gjilan. One of the biggest plants for water is in Perlepnica village and another plant with smaller dimension to supply drink water is in Velekica village. The main issue focuses on the water treatment plant in the Velekica village because the presence of manganese (Mn^{+2}) as metal is always present in six underground springs. Quantity of Mn mg /dm^3 in groundwaters is out of norms allowed under WHO. The presence of this metal forces the water industry to use $KMnO_4$ continuously. In the water the present of this metal is from (0.05-0.0015) mg /dm^3 during 2017 and January 2018 and after the manganese processing process is reduced to (0.11- 0.31) mg /dm^3. While in the water treatment plant in Përlepnica village, there is no problem with heavy metals and the process of processing continues today without any problems.

Keywords: Water industry, Groundwaters, Manganese, Chemical reactor, Oxidation

INTRODUCTION

Water is considered as the most important subject of today and the future in many different environments. Water management includes directly and indirectly many actors and areas of processes related to the use of water. It is clear that no sector or institution alone can afford to achieve equal, fair, peaceful and sustainable use of water resources without working in cooperation. (Cetin 2013; Sevik and Cetin 2015; Cetin 2015: Cetin 2016; Yigit et al., 2016; Cetin et al., 2018).

Shallow aquifers represent water reservoirs for public and private drinking supplies, for irrigation and livestock, and for industrial uses. Therefore, information concerning the geologic nature of such aquifers, the sources and directions of their flows, and their interactions with surface running water is of prime importance. In fact, interactions between sub-surface aquifers and surface run-off waters are often complex and depend on a variety of parameters, which include petrography of the host rocks, shape of landforms, type of climate, but also regional exploitation of the local resources (Clauer et al., 2017).

As a town Gjilan there are two state water treatment plants, one built in the former Yugoslavia in the village of Përlepnica but renovated again by the state of Switzerland and another plant was built by the Swiss state in the village Velekica on the outskirts of the city. The surface water treatment plant in Përlepnica has large processing of capacity when in one dam there are approximately 5 million m3 where the whole water is collected from the atmospheric precipitation, while the water processing plant at Velekica has a small processing of capacity because water is taken underground water as in the (Figure 1) and exactly this plant has serious problem with one ion, which is dangerous for healthy and this is manganese Mn+2, as a consequence of this potassium permanganate is active all the time to reduce the value of this metal by providing water as suitable for drinking, so without water there is life and includes one of the basic and necessary conditions for the existence of life and every industry.

Economic enterprises and all industries supply with water from natural. Of the used water are by sweet surface water including rivers, lakes but during geological research work until now significant groundwater reserves have been discovered, which are of particular importance to the development of the industry, especially in poor regions with other water sources (Agolli, 1983). Manganese Mn^{+2} is present mostly at the end of collecting water reservoirs because the elements fall down due to gravity retraction. Mn (II) is also used as a low catalyst acid-base in some enzymes. Spectroscopic detectors change depending on the oxidation state. Mn^{+2} is not considered a highly dispersed element (Atkins et al., 2014). In order to provide a normal performance of industrial processes, a set of measurements with working parameter values should be performed. The system that operates or intervenes to achieve this goal, regardless of the disorders that may arise during the development of the process, are related to the automatic control system (Pinguli et al., 2017). The manganese oxidation reaction is fast and efficient enough using potassium parabens, but potassium permanganate often also contains chlorine, but its products do not pose any problems, see at the reactions below:

$$2Mn^{+2} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+ \quad (1)$$

$$3Mn^{+2} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+ \quad (2)$$

$$Mn^{+2} + Cl_2 + H_2O \rightarrow MnO_2 + Cl^- + H_3O^+ \quad (3)$$

Chemical reactions in the industries are frequently performed in stirred reactors that are operated at batch, semi-batch, or continuous flow configuration. The choice of the operation configuration is done in the planning stages of the process development. However, if the chemistry of the reaction and its hydrodynamics are not well understood, wrong selection of conditions will be adopted in the process development. Once a process is well known, not only from the chemical aspect, but also from the hydrodynamic aspect (e.g., heat, mass, and momentum transfer), only then is it possible to design an optimal process for production. The reason is that the yields of some diffusion-controlled reactions are highly depended on the hydrodynamic properties (Cheng et al., 2018). In our case the automatic control system has a very good communication with chemical processes occurring in the industry, so mistakes are easily eliminated, failures are very rare. The overall process of an automated system is seen in (Figure 1).

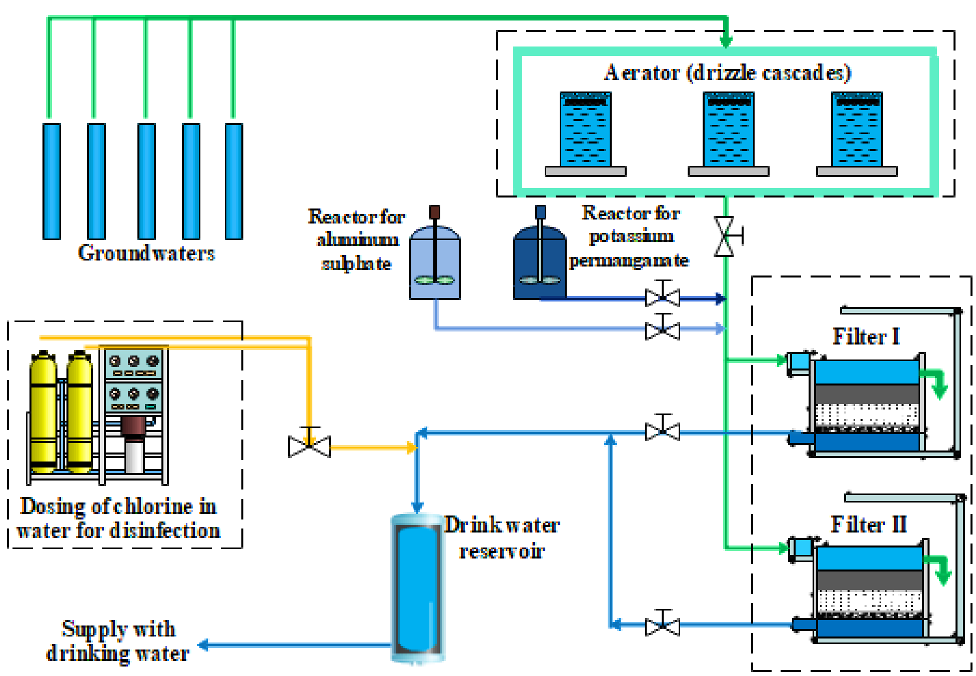

Figure 1. Industrial process of groundwaters treatment in Velekinca plant in municipality of Gjilan

MATERIALS AND METHODS

Preparation of potassium permanganate aqueous solution ($KMnO_4$) for manganese oxidation (Mn)

Although some heavy metals are necessary for biosynthesis in human, excessive amounts may be toxic. Due to their toxicity and non-biodegradability, heavy metals in water seriously threaten aquatic organisms and human health via drinking water as well as food chain pathways. Heavy metal pollution in drinking water is becoming an increasing problem globally, but drinking water resources are the basis of human existence, which should be safe and unpolluted (Yan et al., 2018), so in our case it is necessary to prepare the $KMnO_4$ solution in the chemical rector, which in a very fast way with the automatic flow of the system, to oxidize manganese (Mn) *etc*, importantly, Mn can cause neurotoxicity in humans.

The ideal mix reactor represents an uninterrupted device where the concentration of each component is the same at each point of the volume of the apparatus. In this way, the concertation of each component in effluent in this reactor will be equal with his concertation inside the reactor (Malollari et al., 2017). The chemical reactor is in continuous operation that manganese as heavy metal is oxidized as fast as possible by potassium permanganate ($KMnO_4$). Permanganate potassium in water flow as required, if Mn grows as metal in the nitrogenous water the concentration of $KMnO_4$ increases. Generally, the $KMnO_4$ solution is prepared from (700-1500) gr in the chemical reactor with a capacity of 750 dm^3. Schematic, the ideal mix reactor is shown in (Figure 2).

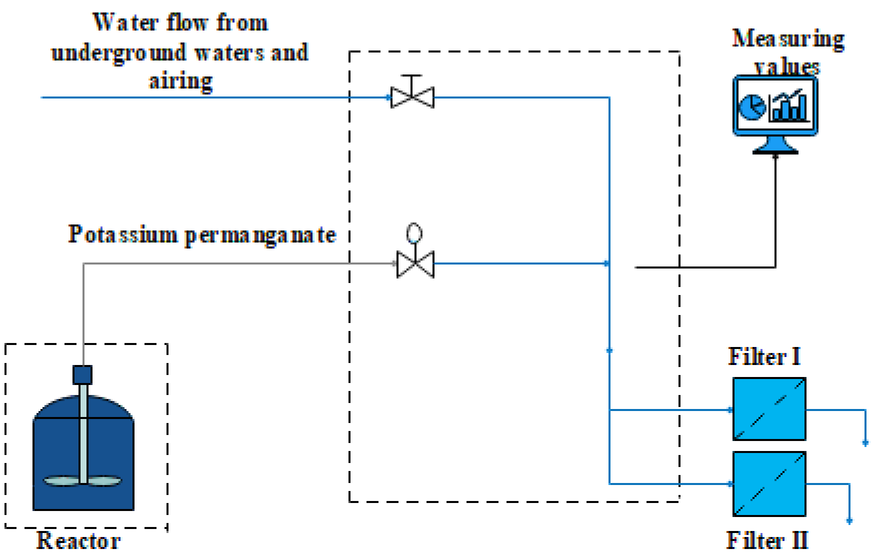

Figure 2. Water solution dosage with $KMnO_4$ for Mn oxidation before water filtration

Chemical properties of potassium permanganate ($KMnO_4$)

Potassium permanganate is a purplish colored crystalline solid. Non-combustible but accelerates the burning of combustible material. If the combustible material is finely divided the mixture may be explosive. Contact with liquid combustible materials may result in spontaneous ignition. Contact with sulfuric acid may cause fire or explosion. Used to make other chemicals and as a disinfectant (URL-1, 2018). Potassium permanganate, or $KMnO_4$, is a common inorganic chemical used to treat drinking water for iron, manganese and sulphur. It can be used as a disinfectant as well, keeping drinking water free of harmful bacteria. Drinking water facilities commonly use potassium permanganate in the early part of the disinfecting process to reduce the amount of later disinfectants, like chlorinated compounds, that must be used (URL-2, 2018).

The method of defining manganese (Mn) and potassium permanganate ($KMnO_4$)

Groundwater geochemistry provides the means to better define the aquifer systems, their water sources, the geochemical evolution as a result of water-rock interaction and gives a unique insight into its dynamics (Calligaris et al., 2018).

Determining $KMnO_4$ is often complicated during titration because it needs high precision. Before titration into an erlenmeyer, put 100 ml of sample water and add approximately 5 ml of H_2SO_4 1/3, then place erlenmeyer in an electric heater. After a short heat we add 15 ml $KMnO_4$ and stand in the electric heater for approximately 10 minutes. After 10 minutes with pipette, add oxalic acid ($H_2C_2O_4$) with a volume of 15 ml with a concentration of 0.05 mol / dm^3 and the solution will boil until staining, then titrate with $KMnO_4$ to a purple colour and read the volume in the burette (Korça, 2013). The formula for $KMnO_4$ calculation uses the equation below:

$$\mathrm{KMnO4}\,\frac{\mathrm{mg}}{\mathrm{L}} = \frac{[(15+V_{KMnO4})*C_{KMnO4}-2*15*0.05/5]*158.04*1000}{V_{mostrës}} \quad (4)$$

Manganese determination method with spectrophotometer

Absorption spectrometry in the ultraviolet and visible region is based on the electromagnetic radiation absorption of molecules in the UV spectra of 160–400 nm and VIS 400–780 nm range. UV-VIS radiation absorption causes the excitation of the electrons of chemical bonds by passing the 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 (Lazo and Çullaj, 2017). The Hach Model DR/2010 Spectrophotometer is a microprocessor-controlled single-beam instrument for colorimetric testing in the laboratory or in the field. The instrument is available for over 120 different colorimetric measurements and allows convenient calibrations for user-entered and future Hach methods (DR/2010 Spectrophotometer instrument manual, 1999). With the instrumental method of using spectrophotometer DR / 2010 for determining Mn, in which this measurement is much faster than through the analytical method. Before the spectrophotometer is worked, blank test should be performed and then the analysis will begin with the 279.5 nm value length program for determining Mn. The sample cell is filled with water to the mark and put the powder reagent, but the reaction time after the program is 5 minutes and should be waved after this time interval, set the reading stone and get the result obtained on the monitor.

RESULTS AND DISCUSSION

Often, classical hydrogeological studies are not enough to shed light on the groundwater hydrodynamics environments, due to the complex flow paths in fracture and karst conduits systems (Calligaris et al., 2018). Water treatment is a very extensive subject involving engineers specializing in drinking water production, so that the results obtained before and after the process are able to comment on their results and the achievements they have made during the process. In our case, we as engineers have been monitoring for many months during 2017 and 2018 by observing this heavy metal in groundwaters before and after the processing process.
During February 2017 the amount of Mn was very high to 0.33 mg /dm^3 and was reduced after oxidation up to 0.02 mg /dm^3, as seen in (Figure 3). In March, the amount of Mn reached 0.27 mg /dm^3, but during the oxidation of Mn, its amount is reduced to 0.02 mg /dm^3. The World Health Organization (WHO) has a special criterion for heavy metals especially for Mn. According to WHO, the value of Mn in water is only allowed at 0.05 mg /dm^3. During May, Mn was 0.28 mg /dm^3 in groundwaters, but when using potassium parchment, the value of Mn was reduced to a very high level at 0.01 mg /dm^3. During the month of June, the atmospheric precipitation is not so present that even Mn as metal in these groundwater decreases its quantity. In this month the amount of Mn is 0.28 mg /dm^3, while the lowest is 0.13 mg /dm^3. During oxidation of this heavy metal its quantity is 0.01 mg /dm^3. In July, the value of Mn is not higher than 0.28 mg /dm^3, while during oxidation the amount of Mn is reduced to 0.01 mg /dm^3. In the month of August, the amount of Mn was no more than 0.28 mg /dm^3 and the reduction of Mn after the process was reduced to 0.01 mg /dm^3, as seen in (Figure 3). So, in July with the month of August, the quantity of Mn as heavy metal was the same and there was no change, while in September the amount of Mn was up to 0.24 mg /dm^3 and during oxidation of this metal the amount of Mn was in 0.04 mg /dm^3, the reduction of Mn in this month has almost been a bit more difficult compared to the other month. In October, the amount of Mn was not higher than 0.24 mg /dm^3, while during oxidation it was reduced to 0.01 mg /dm^3, see (Figure 3). During November, the amount of Mn included this value of 0.22 mg /dm^3 and this value was not very high during this month, in some way did not change the amount of Mn. During oxidation of this metal the amount is reduced to 0.02 mg /dm^3. The amount of Mn in the groundwaters of this industry was higher in October than in November. In December the snow precipitation was very high so that the amount of Mn as heavy metal reached 0.25 mg /dm^3, while during the oxidation of Mn the value has been reduced by oxidation at 0.01 mg /dm^3. In January 2018, the value of Mn was raised to 0.26 mg /dm^3, much more compared to other months. Manganese during oxidation has reached this

month to be reduced to 0.05 mg /dm^3. This value is very close to disagreement with WHO rules. Mn as heavy metal is in accordance at 0.05 mg /dm^3 and this value is acceptable. As a conclusion to these discussions of these results is that during Mn oxidation has done a very good job by greatly reducing Mn and all values obtained after processing are in accord with the WHO regulation, see in (Figure 3).

The potassium permanganate in our case as a user of Mn oxidation is greatly reduced. Reduction of $KMnO_4$ after the process is a very important process during processing because it gives evidence that the higher the $KMnO_4$ reduces, the faster the Mn is oxidized. The quantity of $KMnO_4$ is greatly reduced as seen in the (Figure 4) during the process of processing these underground waters due to the high quantity of Mn.

In the surface water industry in the village of Përlepnica, Gjilan municipality, there is no evidence of a problem with heavy metal such as Mn. Usually in this water processing industry Mn as heavy metal can be present when the dam level drops too low. Usually during the summer season, the atmospheric precipitation is not very high, so the water collection is not very large. In July, when the dam level dropped, the amount of Mn was very high and so $KMnO_4$ was used as an oxidant of Mn. The amount of Mn in this month July was 0.28 mg /dm^3. While throughout the year the quantity of Mn is very low as value and does not express any major concern in comparison with the Velekica underground water treatment plant, see (Figure 5).

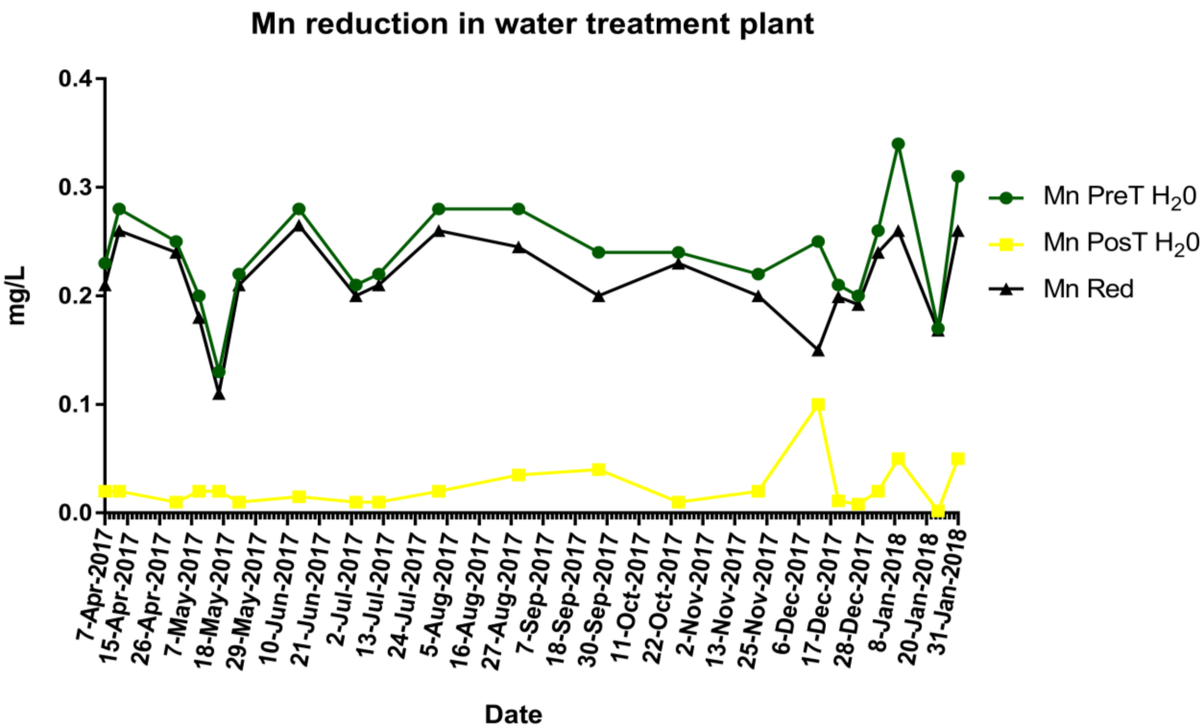

Figure 3. Manganese data (Mn) at the water processing plant in Velekica village

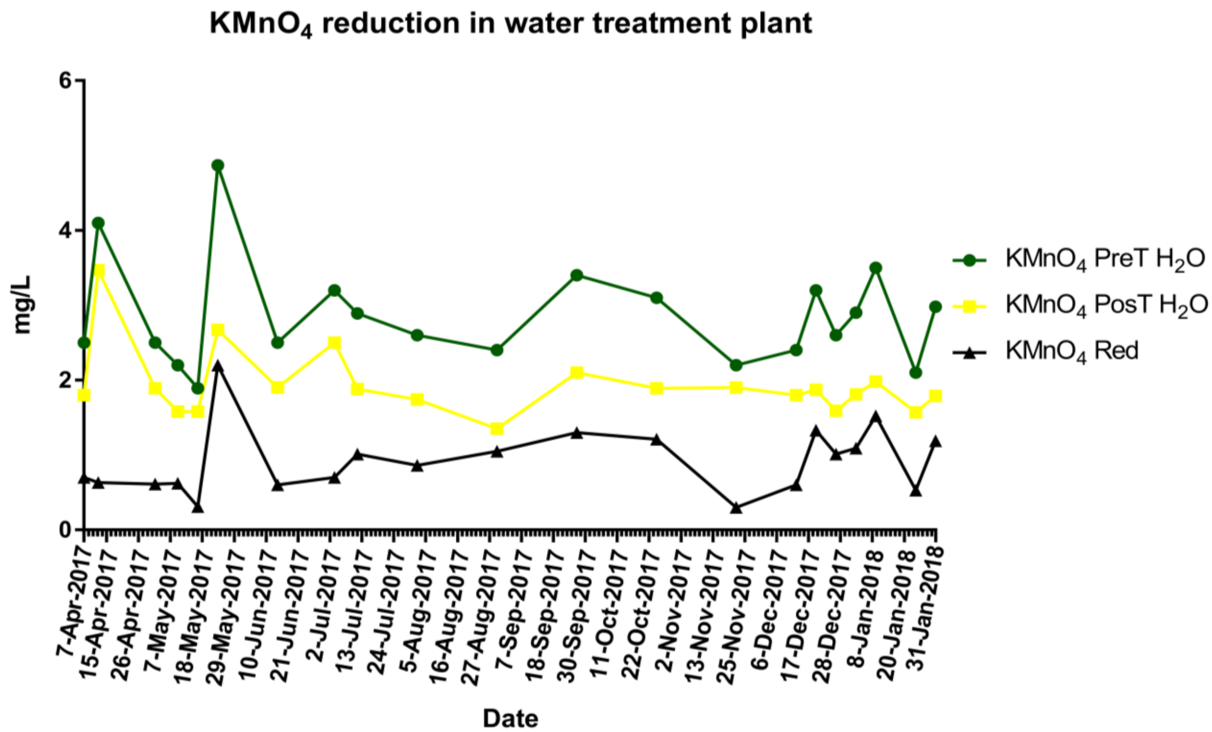

Figure 4. Potassium permanganate data ($KMnO_4$) at the water processing plant in Velekica

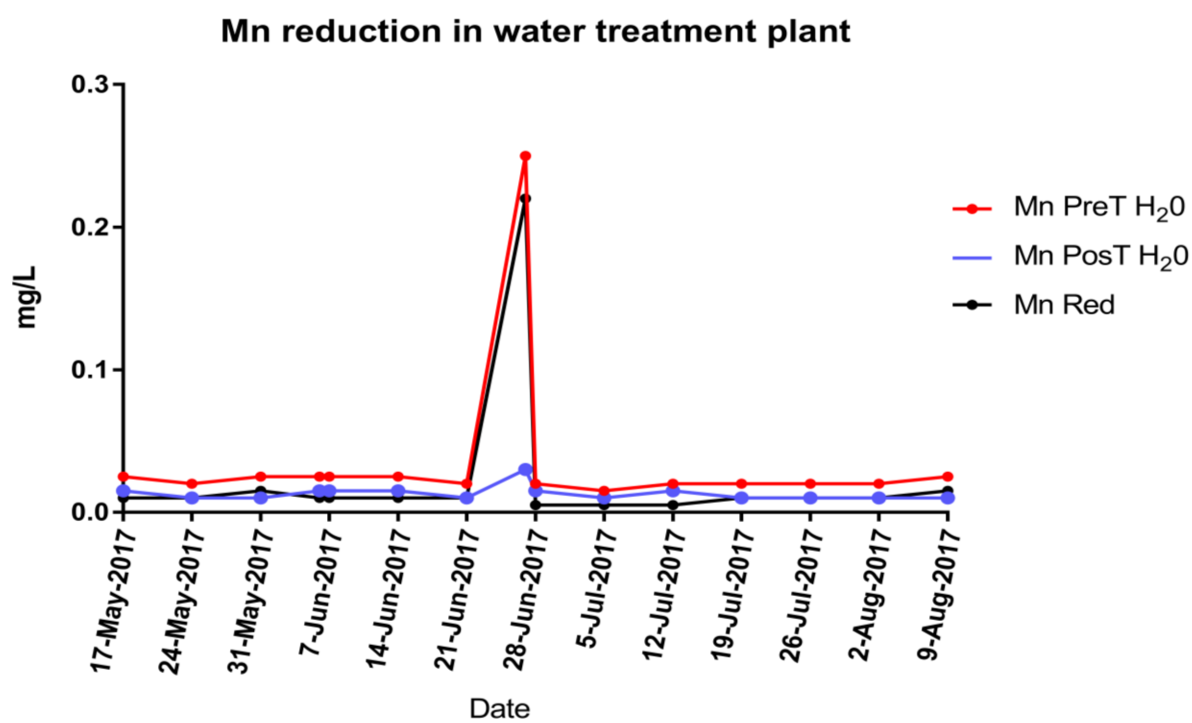

Figure 5. Manganese data (Mn) at the water treatment plant in the village of Përlepnica

CONCLUSION

The site of the water treatment plant in the Velekica village of Gjilan municipality has a major problem with the connection to a heavy metal such as manganese (Mn). This industrial plant is supplied with underground water with a depth of 40 m diameter 70 cm. The analyses involved almost in 2017 send us to the conclusion that the manganese (Mn) before processing its value as metal is very high, but during the processing of these underground springs, the water plant operators have been given special care by reduce the amount of Mn to the permissible levels of WHO and EU for heavy metals and this is a good achievement that is offered to a good quality water service and special care for the health of human health. Regarding the surface water treatment plant in the village of Përlepnica there is a great certainty about the development of the processing process and this is seen in the analyses that we have realized. The world today is increasingly struggling for health security to enjoy ever better health. In the end, these heavy metals in the Velekica industrial plant are very high in Mn and it is also impossible to remove potassium parchment ($KMnO_4$) as heavy metal oxide, such as Mn. $KMnO_4$ is active at all times to oxidize Mn and we have achieved to actually oxidize it and walk with a high work safety in the processing of these groundwaters.

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