U.P.B. Sci. Bull., Series B, Vol. 86, Iss. 1, 2024. ISSN 1454-2331

PRELIMINARY STUDIES OF THE LABORATORY TREATMENT OF SOME UNDERGROUND WATERS

Thaaer Hamed ABED [1], Daniela Simina ȘTEFAN[2], Mircea ȘTEFAN[3]

This paper presents preliminary studies on the removal of sulphide hydrogen, ammonium and organic compounds from groundwater through aeration, biodegradation and adsorption. Natural groundwater taken from a borehole located in the Lehliu Gara area, Calarasi county, was used. The raw water was introduced into an experimental laboratory installation, in three batches. The following parameters were monitored: pH, conductivity, sulphides and sulphide hydrogen, ammonium and total nitrogen, organic compounds, CCOMn, and dissolved oxygen. The experimental laboratory facility was operated for a period of 72 days, when a volume of 110,472 L was passed, during which 436.87 g of ammonium was removed from the 558.49 g entered into the system. From the total amount, 114 g of ammonium (20.4%) were removed by aeration and 436.9 g, i.e. 57.8% of ammonium, were removed by microbiological processes. To remove sulphide hydrogen and ammonium by aeration process, 63.47 m^3 of air, 3 L of quartz sand and a mass of approximately 5 kg were used.

Keywords: groundwater treatment, aeration, adsorption, biodegradation, sulphide hydrogen, ammonium, and organic compounds

1. Introduction

The greatest challenge for water operators is the application of cheap and efficient technologies that ensure the achievement of the specific parameters for drinking water imposed by the new European legislation for drinking water Directive 2020/2184/EC harmonized in Romanian legislation by Ordinance 7/2023 [1]. The classic technologies used in treatment plants are based on processes such as desorption of dissolved gases, peroxidation of dissolved salts and organic compounds, coagulation, flocculation, sedimentation, and filtration for the removing of particles and disinfection to remove microorganisms [2, 3].

Pre-oxidation of reduced compounds like ammonia, sulphide hydrogen and sulphides, is a particularly important step in the water treatment flow. The most used oxidants are: O_2 from air, Cl_2, ClO_2, O_3, hypochlorite, $KMnO_4$, etc. Oxidation

---

[1] PhD student, Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology POLITEHNICA of Bucharest, Romania, e-mail: thaaerabed85@gmail.com

[2] Prof., Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology POLITEHNICA of Bucharest, Romania, e-mail: daniela.stefan@upb.ro

[3] Associate professor, "Titu Maiorescu" University, Pharmacy Faculty, Bucharest, Romania

with chlorine compounds can result in toxic chlorinated compounds, trihalomethanes, for which concentration limits have been imposed. Therefore, changes are needed in the technological flows to limit the use of chlorine compounds [4-7]. From the oxidation processes there can result in colloidal particles that are removed from water by coagulation-flocculation processes, using coagulants such as aluminium sulphate, ferric chloride, aluminium polychloride, etc., and polyelectrolytes such as polyacrylonitrile. Filtration can be done on silica sand, manganese greensand, iron sand, sand/anthracite, ceramic, etc. Activated carbon, chlorination (for the destruction of bacteria, algae, and fungi in the treatment plant), or ozonation are used to remove organic compounds [3, 8-14].

H_2S has the unmistakable smell of spoiled eggs. The specific odour of water containing H_2S is felt at concentration values between 0.025 - 0.25 µg H_2S/L. In water, it is provided by natural and anthropic activities, by aerobic or anaerobic degradation of organic and inorganic compounds with sulfur. Sulphide hydrogen from water is a sum between many species like free sulphide that includes a dissolved gas [$H_2S(g)$] and it dissociated ions, bisulphide (HS^-) and sulphide (S^{2-}), and complex sulphides as dissolved metal–sulphide complexes [15].

The presence of H_2S in water is harmful to health when water is transported in lead pipes because the lead sulphide formed is soluble and can determine lead poisoning. Copper pipes can also be attacked by sulphides-containing waters. [16].

Sulphide hydrogen can be removed by aeration (gas transfer), and above the carbon filters, by cascade aeration, and in concentrations lower than 1-2 mg/L by spraying; in the same process, oxygen is simultaneously added to the water.[16]

NH_4^+ cation is present in natural surface waters and wastewater. NH_4^+ concentrations of groundwater are low because it is absorbed by soil particles and clays and does not spread easily through infiltration. NH_4^+ results from the deamination reactions of nitrogen-containing organic compounds and from the hydrolysis reaction of urea:

$$(NH_2)_2\,CO + 2H_2O \longrightarrow (NH_4)_2\,CO_3$$

The presence of ammonium (NH_4^+- N) in water causes high levels of chlorine required in the disinfection operation, which leads to the formation of trihalomethanes or other organochlorine substances that have been proved to be carcinogenic [17].

In the presence of oxygen, the organic substance can be decomposed aerobically, resulting carbon dioxide and ammonia. 1.4 g of O_2 is required for 1 g of organic substance, producing 0.16 g of NH_4^+. For oxidation of 1 g of NH_4^+, 3.6 mg O_2/mg NH_4^+ are required. The oxidative process can occur in the presence of oxygen directly or mediated of microorganisms. Simple filtration through quartz sand contributes to the removal of iron and manganese, organic substances, and ammonium by nitrification. By conventional rapid filtration, ammonium is removed in concentrations of 2-3 mg/L. When raw water (usually groundwater) has ammonium in higher concentrations, double filtration with intermediate aeration is a solution that gives good results [18-20].

This paper presents preliminary studies on the removal of hydrogen sulfide ions, of ammonium and organic compounds from groundwater through aeration, biodegradation, and adsorption. Natural groundwater taken from a borehole located in the area of Lehliu Gara village, Calarasi county, was used. The raw water was introduced into an experimental laboratory installation, in three batches.

2. Materials and methods

The raw water used in these studies was characterized by concentrations of ammonium, sulphides and sulphide hydrogen parameters and organic compounds having values above the maximum admissible limits. The values of maximum admissible limits (MAL) for interest parameters are presented in Table 1.

Table 1

No.	**Parameter name**	**MAL, RO Ordonance 7/2023**	**MAL, 2020/2184 Directive**	**MAL, US EPA**	**MAL, WHO (World Health Organization)**	**MAL, Iraqi Legislation**
1	Conductivity	2500 µS cm^{-1}	2500 µS cm^{--1}			700 µS cm^{-1}
2	Iron	200 µg/L	200 µg/L	-	300 µg/L	300 µg/L
3	Manganese	50 µg/L	50 µg/L	-	0.1 µg/L	0.1 µg/L
4	Sulphides	100 µg/L	-	-	-	0.1 µg/L
5	Ammonium	0.5 mg/L	0.3 mg/L	-	-	0.2 mg/L
6	Nitrate	50 µg/L	50 µg/L	10 µg/L	45 µg/L	50 µg/L
7	Nitrite	0.5 µg/L	0.5 µg/L	1 µg/L	3.2 µg/L	3 µg/L
8	Oxidability Permanganate index	5 µg O_2/L	5 µg O_2/L	-	-	5 µg/ O_2/L
9	Sodium	200 µg/L	200 µg/L	-	-	200 µg/L
10	pH	$6.5 \leq pH \leq 9.5$	$6.5 \leq pH \leq 9.5$	-	-	$6.5 \leq pH \leq 8.5$
11	Sulphate	250 µg/L	250 µg/L	-	-	250 µg/L

In Fig. 1 the pilot installation used in the experiments was shown.

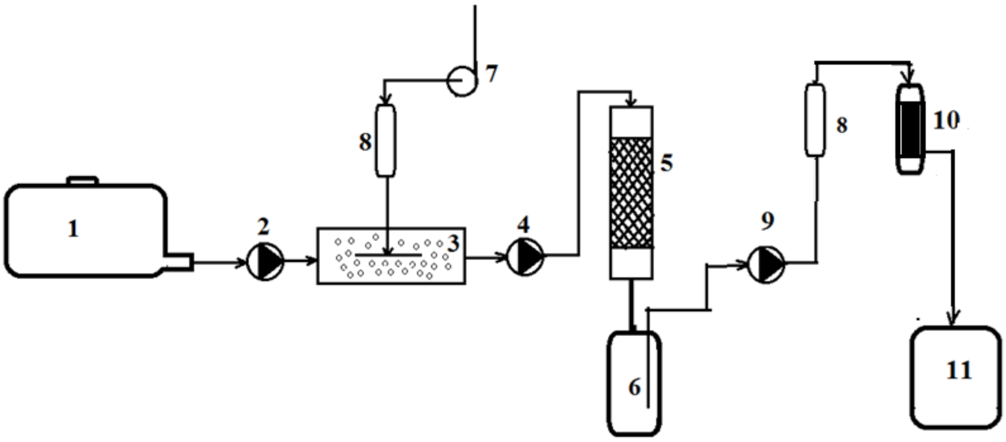

Fig. 1. Water treatment laboratory installation

The raw water is stored in water tank 1, from which it is pumped by peristaltic pump 2 into the aeration basin 3. The water supply flow in the aeration basin is 6 l/hour. From the aeration basin, the water is pumped by pump 4 into filter column 5. The water is filtered through the square sand column with a height of 550 mm and a diameter of 45 mm, where the sulfur formed by oxidation and microbiological degradation processes take place. of compounds with sulfur and nitrogen. Treated water is collected in basin 6. Air is pumped into the aeration basin with pump 7. The flow of pumped air is measured with an air rotameter. The pumped air flow rate is about 180 L/h. It was measured with the air rotameter 9. The water in tank 6 is pumped with the pump 8' in the adsorption column with active carbon 10. The treated water is collected in tank 11.

The initial characterization of the water was carried out during the treatment process in the treatment laboratory installation through aeration and microbiological degradation on a filtering layer of quartz sand. Samples were taken at the entrance to the installation (called input), after the aeration basin (called aeration), at the exit after the sand layer (called filtration), and after the adsorption column (called output). The values were compared with the maximum admissible limit value, MAL.

Parameters were determined as following: pH, using Janway pH-meter, concentration of hydrogen sulfide and sulfides, using kits from HACH Langhe type LCK – 032, ammonium content, using kits LCK-304, conductivity, using Janway conductometer, nitrogen content with kits HACH Langhe LCK 339 and total nitrogen with HACH Lange LCK238 kits, dissolved oxygen content using a selective electrode method, using Janway oximeter. To determine the parameters with kits, (was used) a Spectrophotometer DR3900 was used. To determine the content of organic compounds, the concentration of oxygen produced from the reaction between potassium permanganate in an acidic environment, CCOMn expressed as mg $KMnO_4$/L or mg O_2/L was determined. The experimental laboratory installation was operated for a period of 72 days. The experimental results are presented in Figs. 2-19.

3. Results and discussion

The results obtained after water treatment in the pilot laboratory installation for the first batch of water are presented in Figs. 2 - 7. The initial values of the pH were below 8.5 and, as a consequence of the processes of oxidation and biological degradation, it increased above 8.5, but not more than 8.75. These values are below the admissible limit value of 9.5 imposed by the legislation in force.

The initial conductivity of the water sample was of 925 µS cm^{-1}, and after the start of the experiments, there was a decrease in conductivity, due to the desorption of hydrogen sulfide. The conductivity at the exit from the biological oxidation system decreased during the first 75 hours of operation, after which it started to increase slightly. This phenomenon is correlated with the weak increase in the concentration of organic compounds. The values are far below the maximum admissible limit value of 2500 µS cm^{-1}.

The concentration of organic compounds is below the maximum admissible limit. The concentration of dissolved oxygen in the underground water at the entrance (to)/in the experimental installation is very low, close to zero, a few hours after sampling, and increases as it sits in the laboratory. After aeration, the concentration reaches values above 6 mg/L.

The ammonium ion concentration (initially) has initially values of 6 mg/L, 7 times higher than the maximum admissible limit, and gradually decreases to values lower than the MLA after aeration, filtration, and adsorption, after more than 40 hours of operation. (to values lower than the MLA). From the analysis of Fig. 7, it can be observed that there is a variation in the concentration of total nitrogen. It proves that there is a loss of nitrogen in the system, which can be other than in the form of ammonium during aeration and adsorption, or gaseous nitrogen after filtration under the action of microorganisms.

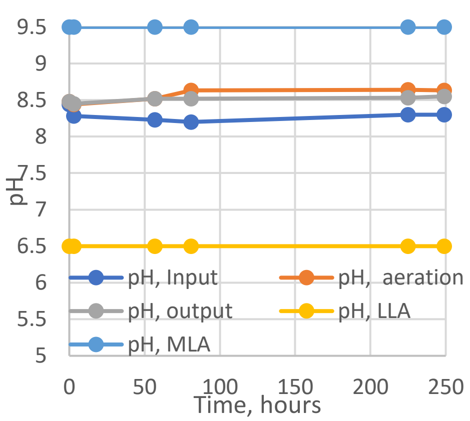

Fig. 2. Variation of the pH values

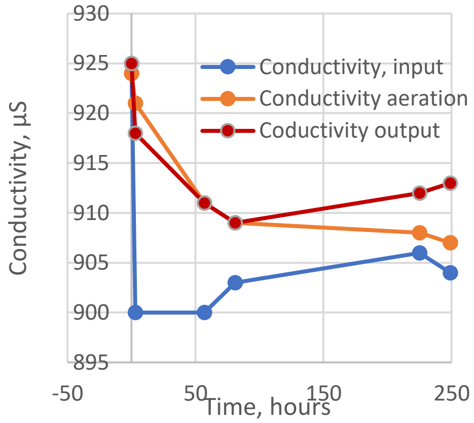

Fig. 3. Variation of the conductivity values

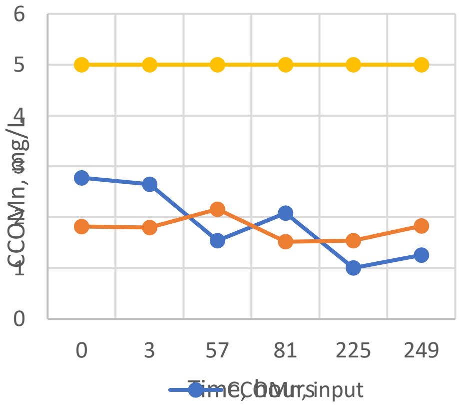

Fig. 4. Variation of the CCOMn concentration

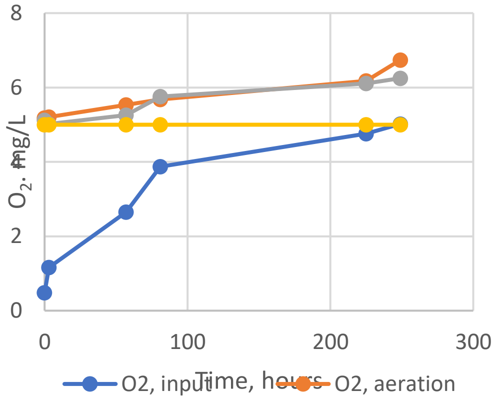

Fig. 5. Variation of the O_2 disolved concentration

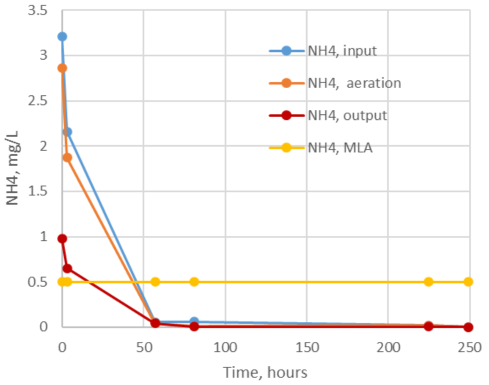

Fig. 6. Variation of the ammonia concentrations

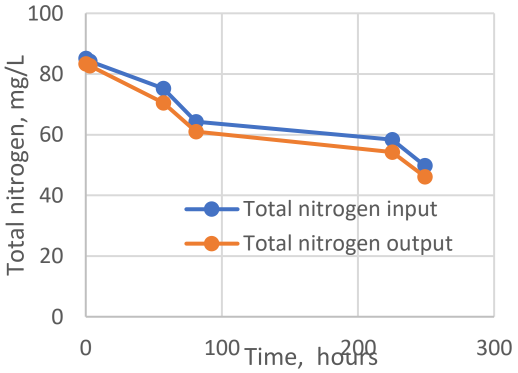

Fig. 7. Variation of the total nitrogen concentrations

The results obtained after water treatment in the pilot laboratory installation for the Second batch of water are presented in Figs. 8 - 13.

The values of the dissolved oxygen content increased in the aeration vessel, reaching around 5 mg/L, which proves that the aeration is efficient, and decreased at the exit from the microfiltration column, which shows that it is consumed in the column, i.e. they take place oxidative redox processes.

The concentration values of organic compounds decreased from the entry into the installation to the exit from the installation, the values are below the permissible limit value of 5 mgO_2/L for Batch 1 - well 1. Regarding Batch 2, the concentration of organic compounds is higher than the maximum admissible limit both at the entrance and at the exit, a fact which requires completing the installation with an adsorption column for organic compounds. It can also be observed that the CCOMn increases at the exit from the quartz sand column, due to the activity of the microorganisms present at this level.

The total nitrogen concentration decreased from the level of the feed vessel in the aeration installation, and slightly, at the level of the biological degradation processes on quartz sand. A decrease in total nitrogen concentration at the exit from the aeration installation is observed, a fact which can be explained by the partial desorption of ammonia through aeration.

The initial concentration of sulphide hydrogen for both batches had values around the permissible limit and fell below the maximum permissible limit (after)/ in the first days after the application of aeration.

Ammonium is a parameter that undergoes changes during the process. It is observed that, after two weeks of continuous operation of the installation, values below 0.5 mg/L are reached. This proves the effectiveness of the microbiological layer that has developed on the sand grains. During the experiments, it was observed that the sand layer became loose in the 4-5 days after the start of the experiments. The nitrate concentration for the second batch (representative of the experiments performed) increased from the entrance in the installation to the exit from the installation. This proves the efficiency of the biological oxidation processes that take place at the level of the microfiltration column. The nitrogen concentration at the exit from the column does not exceed the maximum admissible limit value.

In conclusion, the aeration installation correlated with that of ammonium oxidation proves to be efficient.

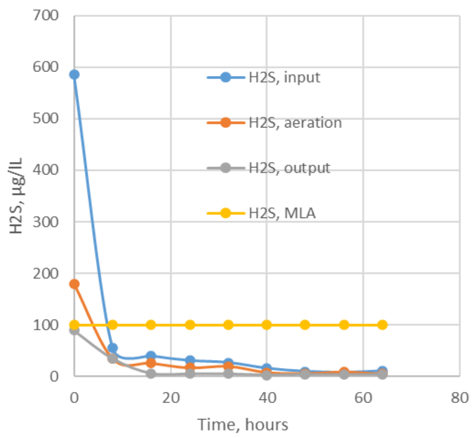

Fig. 8. Variation of the H_2S concentrations

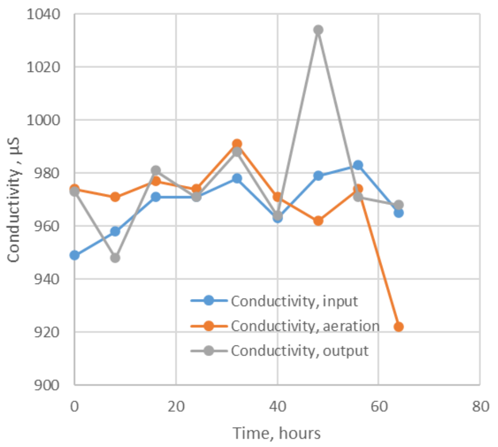

Fig. 9. Variation of the conductivity values

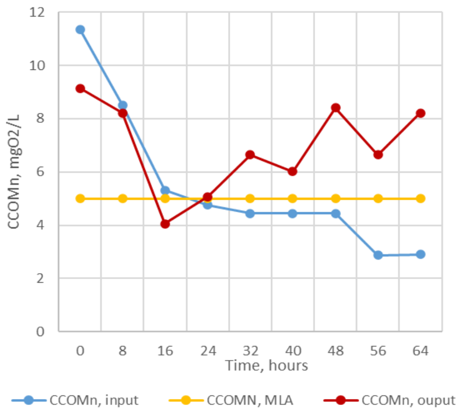

Fig. 10. Variation of the CCOMn concentration

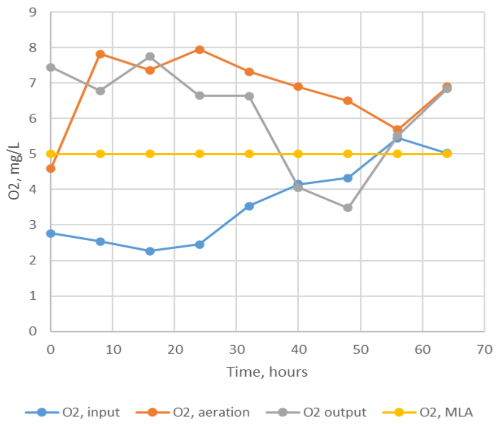

Fig. 11. Variation of the O_2 disolved concentration

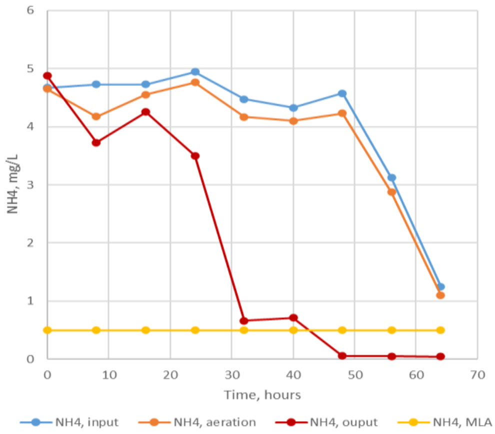

Fig. 12. Variation of the ammonia concentration

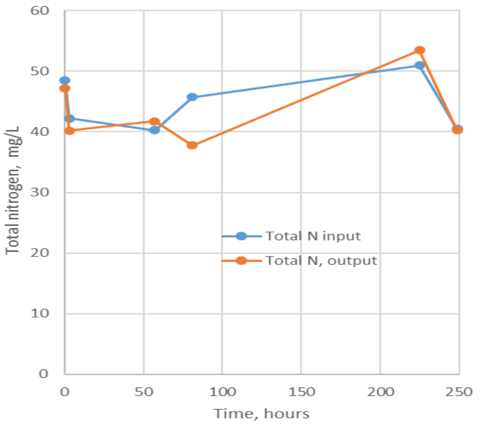

Fig. 13. Variation of the total nitrogen concentration

The results obtained after water treatment in the pilot laboratory installation for the Third batch of water are presented in Figs. 14 - 19. Work was carried out over a period of 33 days, 8 hours a day. The initial pH values were above 7.5 and below 8.7, and following the oxidation and biological degradation processes, it increased above 8.5, but not more than 8.75. These values are below the admissible limit values of 9.5 imposed by the legislation in force (see Fig. 19).

The initial conductivity was of 879 µS, after which it increased both in the aeration basin and at the exit from the sand column, this phenomenon being correlated with the weak increase in the concentration of organic compounds, because of the activity of microorganisms (see Fig. 15).

The content of organic compounds in the water at the entrance and during the experiment has values higher than the maximum admissible limit of 5 mg/L, as it can be seen from Fig. 16. Fluctuations in the concentration at the entrance occur (due to)/ because the fact that the water has a long period of stationary in the laboratory, during which the physical-chemical characteristics are changing. A decrease in concentration compared to the start of the experiment is observed when the water has characteristics close to those existents at the exit from the natural source. At the exit, sometimes the concentration of organic compounds is higher than at the entrance, due to the synthesis of organic compounds by the microorganisms developed on the sand column.

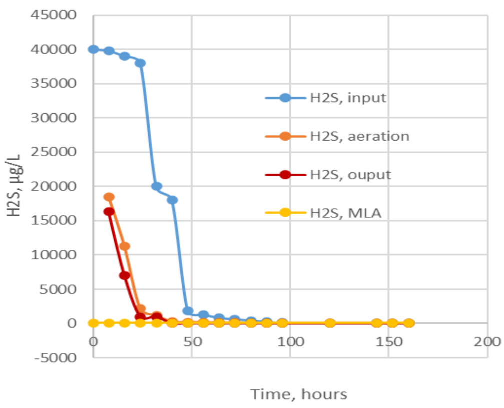

Fig. 14. Variation of the H_2S concentrations

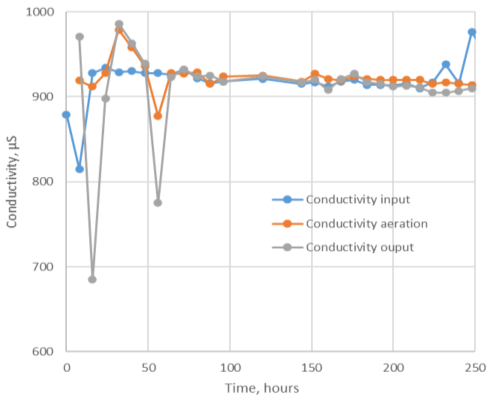

Fig. 15. Variation of the conductivity values

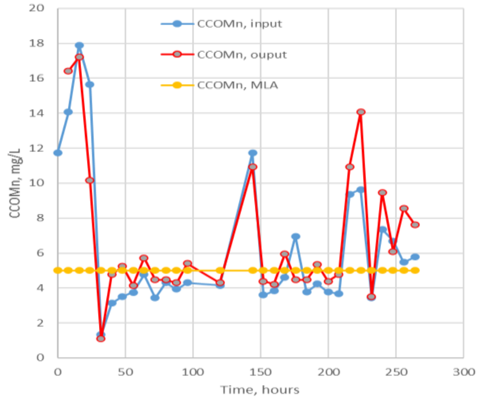

Fig. 16. Variation of the CCOMn concentration

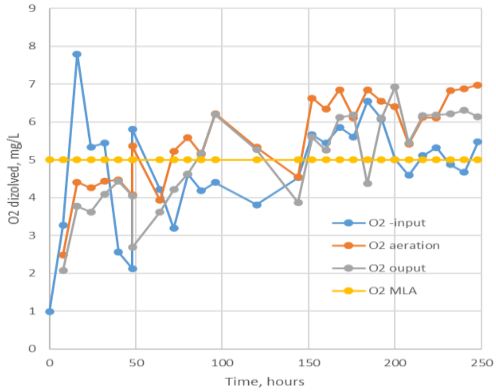

Fig. 17. Variation of the O_2 disolved concentration

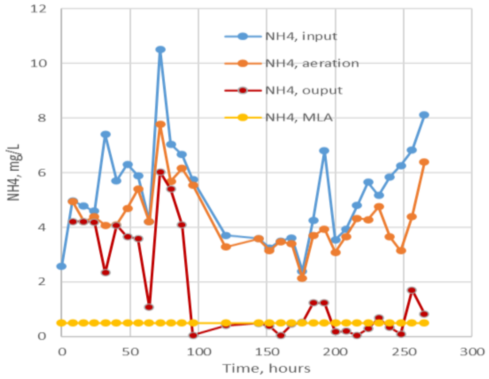

Fig. 18. Variation of the ammonia concentrations

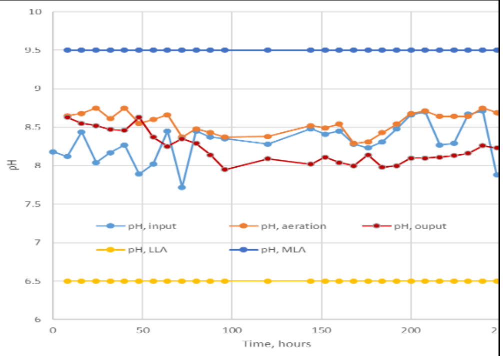

Fig. 19. Variation of the pH values

The hydrogen sulphide concentration at the entrance in the laboratory installation was of 40 mg/L (see Fig. 14). This particularly high concentration was only partially removed in the first days of the experiment, reaching a concentration of 18.5 mg/L after aeration, and 16.5 mg/L after the quartz sand column. The aeration ensured dissolved oxygen concentrations in a range of 4-8 mg O_2 /L, that was not sufficient to ensure the removal of high concentrations of hydrogen sulphide (see Fig. 17). As the water samples settled, hydrogen sulfide was desorbed, and we found that, at initial concentrations of H_2S and sulfides lower than 18 mg/L, aeration became efficient and hydrogen sulfide was removed to values below the LMA, of 0.1 mg /L. At very high concentrations of hydrogen sulphide, it is recommended to use much higher concentrations of dissolved oxygen, in order to have an efficient process.

The initial ammonium content was higher than the maximum admissible limit, reaching over 10 mg/L at the entrance. During the processes, we observed a decrease in the concentration of ammonium in the aeration basin, which proves that there is also a desorption of ammonia through aeration, and in the microbiological degradation column with quartz sand, the removal of ammonia occurs at values below the maximum admissible limit, of 0.5 mg/L. One can see in Fig. 18 that, after 12 days from the start of the process, the microbiological film becomes effective. In order to better understand how the processes took place in the quartz sand column, we must say that the installation did not work between the three bursts. The reactivation of the microbiological activity was achieved after a few days, the efficiency of the microbiological layer was better or worse, batch 1, where the ammonium ion concentration was around 2 mg/L, the biofilm reached the required efficiency after 1 day, for the second batch, where NH_4^+ had a concentration of around 5 mg/L, the biofilm reached the required efficiency after 5 days, and for a concentration of 10 mg/L (Third batch), the biofilm became effective after 12 days. This variation in efficiency can be compensated by increasing the aeration level.

6. Conclusions

Based on the experimental results carried out, it is possible to evaluate the effective values of the desorption processes by aeration and microbiological degradation during the ammonium ion removal process for Batches 1, 2 and 3. The weight of the desorption processes by aeration varies between 0.1 and 50%, the usual values vary in the range of 8-24%, with an average weight of 20.4%. Microbiological degradation processes have a weight between 14-90%, the usual weight being between 30-70%, and the average weight is of 57.80%.

The sulphide hydrogen and ammonia removal facility was operated for a period of 72 days, when a volume of 110.472 L was passed, during which 436.87 g of ammonium was removed from the 558.49 that entered the system. From the total amount, 114 g of ammonium (20.4%) were removed by aeration, and 436.9 g, i.e. 57.8% of ammonium, were removed by microbiological processes. To remove hydrogen sulphide and 114 g of ammonium by aeration, 63.47 m^3 of air, a volume of 3 L of quartz sand and a mass of approximately 5 kg were used.

REFERENCES

[1]. Directive (EU) 2020/2184 on the quality of water intended for human consumption (recast), Directive (EU) 2020/2184 of the European Parliament and of t... (europa.eu).

[2] *C. Teodosiu*, Tehnologia apei potabile și industriale, Ed. Matrix Rom, București, 2001, pag 183-184.

[3]. *M. Sandu, G. Racovițeanu*, Manual pentru inspecția sanitară și monitorizarea calității apei în sistemele de alimentare cu apă. Ed. Conspress, 2006, pag 100-102.

[4]. *A.R. Scott*, Aeration in Water Quality and Treatment, McGraw-Hill Book Co., New York, 1971.

[5]. WHO, World Health Organization, Trihalomethanes in Drinking-Water, Guidelines for Drinking-water Quality, 2004, Microsoft Word - Trihalomethanes.doc (who.int).

[6]. *E. Goldnik, T. Turek,* Removal of hydrogen sulfide by permanganate based sorbents: Experimental investigation and reactor modeling, Chemical Engineering Science, **vol. 151**, 2016, 51-63.

[7]. *U. von Gunten*, Oxidation Processes in Water Treatment: Are We on Track?, Environmental Science & Technology, **vol. 52**, 9, 2018, 5005-5518.

[8] *T. Peitchev*, Characteristics of the processes in rapid sand filters used by the treatment of ground and terrace waters, Water Supply, **vol 9,** 1991, S47–S51

[9]. *Al. Manescu, M. Sandu. Ov. Ianculescu,* Alimentări cu apă, Ed. Didactică și Pedagogică, București, 1994, 285-288.

[10]. *T. Manasfi*, Chapter Four-Ozonation in drinking water treatment: an overview of general and practical aspects, mechanisms, kinetics, and byproduct formation, Comprehensive Analytical Chemistry, vol 92, 2021, 85-116.

[11]. *S. Lim, J. L. Shi, U. von Guten, D. L. McCurry,* Ozonation of organic compounds in water and wastewater: A critical review, Water Research, **vol. 213**, 2022, 118053.

[12]. *C. S. Lee, J. Robinson, M. Fong Chong,* A review on application of flocculants in wastewater treatment, Process Safety and Environmental Protection, **vol. 92, 6**, 2014, 489-508

[13]. *F. Çeçen, Ö. Aktaş,* Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment, 2012, Print ISBN:9783527324712 |Online ISBN:9783527639441 |DOI:10.1002/9783527639441, Ed. Wiley-VCH Verlag GmbH & Co. KGaA;

[14]. *J. Q. Jiang,* The role of coagulation in water treatment, Current Opinion in Chemical Engineering**, vol. 8,** 2015, 36-44.

[15]. *M. S. Wiener, B. V. Salas, M. Quintero-Nu´n˜ez and R. Zlatev,* Effect of H_2S on corrosion in polluted waters: a review Corrosion Engineering, Science and Technology, **vol 41**, 3, 2006, 221,

[16]. *K. Höll,* Water Examination, Assessment, Conditioning, Walter de Gruyter, Berlin, New York, 1972.

[17]. EC-Official Journal the European Communities, “Drinking water Quality Intended for Human Consumption, Brussels, Belgium L330/32 Council Directive 98/83 EC, 1998.

[18]. *T. Stembal, M. Markic, N. Ribicic, F. Briskia, and L. Sipos,* “Removal of ammonia, iron and manganese from groundwaters of northern Croatia – pilot plant studies” Process Biochemistry, **vol 40**, 2005, 327–335.

[19]. *A.G., Tekerlekapoulou, P.D.G. Papazafiris, and D.V. Vayenas*, A full scale trickling filter for the simultaneous removal of ammonium, iron and manganese from potable water”, Journal of Chemical Technology Biotechnology, **vol. 85**, 2010.

[20]. *A.G., Tekerlekopoulau, S. Pawlou, D.V. Vayenas,* “Removal of Ammonium, iron and manganese from potable water in biofiltration units: a review”, Wiley Online Library, 2013.