

Iron and manganese removal from difficult ground water sources

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(Accepted 11 October 2013; Published online 26 December 2013)

Abstract

A large part of the ground water sources from Romania contains iron and manganese in concentration higher than the limits for drinking water. The presence of iron and manganese in drinking water in high concentration determine color in the water and metallic taste. The paper presents the pilot plant studies performed in the Technical University of Civil Engineering of Bucharest, having the scope of iron and manganese removal from two ground water sources. One of the sources is more complex and contains also ammonia, which complicates the treatment procedures. The results of the experimental trials revealed that iron can be removed by oxidation with air and rapid sand filtration up to concentration of 0.01 mg/l in the treated water, but for manganese removal to concentration lower than 0.05 mg/l in the treated water it is necessary to add potassium permanganate as complementary oxidant. When the raw water contains iron, manganese and also ammonia, the treatment scheme is more complicated, the most important criteria for obtaining good quality drinking water are:

- *The order of the processes: iron and manganese removal come first and ammonia removal secondly;*
- *Use of combined oxidation process by air and also potassium permanganate enhance the manganese removal;*
- *Break-point chlorination represents an efficient procedure for ammonia removal. Though, the high chlorine dose determines a risk related to THM formation, fact which requires an adsorption on GAC. Another important aspect is that sufficient reaction time has to be achieved, recommendable one hour.*

Rezumat

O mare parte din sursele subterane de mica sau de mare adancime contin fier si mangan in concentratii care depasesc limitele impuse pentru apa potabila. Prezenta fierului si manganului in apa potabila confera apei culoare iar la concentratii ridicate gust metalic. Articolul prezinta cercetarile efectuate in cadrul Universitatii Tehnice de Constructii Bucuresti in scopul indepartarii fierului si manganului din doua surse de apa subterana. Una dintre surse este mai complexa, contine amoniu ceea ce complica procedeele de tratare. Rezultatele experimentale au aratat ca fierul poate fi retinut prin oxidare cu oxigenul din aer si filtrare pe nisip cuarzos pana la concentratii de 0.01 mg/l in apa tratata, insa pentru retinerea manganului pana la concentratii mai mici de 0.05 mg/l in apa tratata este necesara adaugarea permanganatului de potasiu, ca oxidant suplimentar. In situatiile in care apa bruta contine atat fier si mangan cat si amoniu, schema de tratare este mai complicata, cele mai importante criterii pentru obtinerea unei bune calitati a apei potabile sunt:

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- *ordinea proceselor: indepartarea fierului si manganului in prima faza si oxidarea amoniului in faza a doua;*
- *utilizarea unor procese de oxidare combinate cu utilizarea aerului si a permanganatului de potasiu care imbunatatesc eficienta de reducere a manganului;*
- *clorinarea la break-point reprezinta un proces eficient pentru reducerea amoniului. Deoarece doze mari de clor determina un risc privind formarea THM este necesara adsorbtia pe CAG. Un alt aspect important este un timp de reactie suficient, recomandabil o ora.*

Keywords: iron, manganese, ammonia, water treatment.

1. Introduction

The experimental researches were performed on a pilot plant for the water sampled from two ground water sources: Fetesti and Tandarei. It should be mentioned that the quality of both sources reveal iron and manganese over the limits. In Tandarei ammonia concentration are also over passed, which generates even more difficulties in the treatment process.

The localization of the water sources is presented in Fig. 1.



Figure 1. Water sources localization (source: <http://www.rotravel.com>).

The first step in iron removal will be based on oxidation of the divalent iron using oxygen provided from the air [1,2]. If necessary, it can be supplemented by adding a number of other treatments such as: pH correction, chemical oxidation, flocculation, clarification. Ozone and potassium permanganate are the best supplementary oxidants, especially when complex iron is present. When the water contains high levels of organic matters and manganese, the amount to be dosed is to be identified experimentally if possible.

Manganese Mn^{2+} is very slowly oxidized by oxygen to form MnO_2 . The manganese dioxide will react as catalyst. However, this effect will not be enough to produce treated water that is completely manganese free.

In practice, instead of "manganising" sand, it is advisable to use a filtration media of MnO_2 (green manganised sand) that can be mixed in greater or lesser amounts with the regular sand and which will also require regeneration at regular intervals.

Ammonia removal can be reached by biological processes or by oxidation chlorine when the

amount of chlorine dosed rises above the critical point. However, disinfection by-products (chlorinated compounds, THMs) often appear when precursors (natural organic matter - NOM) occur in raw water. The presence of THMs in drinking water is not desirable due to high carcinogenic risk. Therefore, this technique only applies when the raw water contains low amounts of precursors (NOM).

Chlorine is the single effective chemical for elimination of nitrogen ammonia present in the raw water in the molecular form NH_3 , but also in the ionic form NH_4^+ .

2. Materials and methods - description of the pilot plant

A pilot plant belonging to the Faculty of Hydrotechnics, UTCB was used for the research. The main characteristics of the pilot plant are:

- pre-oxidation contact tank, having a water column height of 4 m; different contact times can be provided in the range of 8 – 30 min.;
- rapid sand filter, with a mono-granular layer having the height of $H=1.2\text{m}$; the filtration velocity can be varied from 4 m/h to 15 m/h;
- chemical preparation and dosing which includes dosing pumps and storage tanks;
- treated water reservoir having the volume of $V=300\text{ dm}^3$;
- backwash water installation consisting of reservoir, backwash water pump and air blower.

Several oxidizing agents have been used during the experimental trials: compressed air, potassium permanganate and sodium hypochlorite. Fig. 2 presents an image of the plant.



Figure 2. Water Treatment Pilot Plant, UTCB.

3. Results and discussions

3.1 Assessment of the raw water quality

The evaluation of the raw water quality was performed in several stages of sampling from both sources (Fetesti and Tandarei). The average values are presented in Table 1.

Table 1. Raw water quality

Item	Parameter	Unit	Fetesti Source	Tandarei Source	Maximum admissible values*
1	pH	units	7.82	8.05	6.5 – 9.5
2	Conductivity	μS/cm	745	1249	2500
3	Alkalinity	mequiv/l	5.5	6.1	-
4	Total hardness	Hardness degrees	16.52	21.28	min. 5
5	Calcium	mg/l	64	84	-
6	Magnesium	mg/l	32.8	41.31	-
7	Ammonia	mg/l	0	0.88	0.5
8	Nitrates	mg/l	7.4	1	50
9	Bicarbonates	mg/l	335.5	372.1	-
10	Chlorides	mg/l	131.35	132.06	250
11	Iron	mg/l	0.17	0.24	0.2
12	Manganese	mg/l	0.140	0.156	0.05
13	Sulphates	mg/l	26	116	250
14	Organic matter	mg KMnO ₄ /l	1.12	2.21	20
15	Total organic carbon	mg/l	1.6	2.9	no abnormal changes and acceptable to consumers
16	Turbidity	NTU	0.76	0.7	1
17	Arsenic	μg/l	<0.2	<0.2	10
18	Cadmium	μg/l	<0.4	<0.4	5
19	Total chromium	μg/l	<0.5	<0.5	50
20	Copper	mg/l	<0.0006	<0.0006	0.1
21	Mercury	μg/l	<1	<1	1
22	Lead	μg/l	<1	<1	10

Note: * Maximum admissible values, according to the Drinking Water Law (458/2002, 311/2004) [4] and EU Directive 98/83/EC, 1998 [3].

The raw water analysis reveals the following:

- Both sources correspond to the required drinking water quality, except the following:
 - For Fetesti the manganese concentration registers 0.14 mg/l compared to the maximum admissible value of 0.05 mg/l;
 - For Tandarei several parameters are over passed:
 - The ammonia concentration registers a value of 0.88 mg/l versus 0.5 mg/l – the maximum admissible value;
 - The iron concentration registers a value of 0.24 mg/l versus 0.2 mg/l – the maximum admissible value;
 - The manganese concentration registers a value of 0.156 mg/l versus 0.05 mg/l – the maximum admissible value;
- Both sources register low TOC concentrations, fact which reveal that the THM formation potential is consequently low and chlorination is a viable process;
- The mineralization is normal for both sources;
- The pH registers neutral to light alkaline values in both sources.

3.2 Experimental trials on Fetesti water source

For the Fetesti source there were performed two experimental trials according to the treatment schemes presented in the Fig. 3. Both schemes are conventional treatment schemes for iron

removal. The main difference between the schemes consist of iron oxidation which has been made using air in the first trial while in the second experimental trial it has been used air + KMnO_4 .

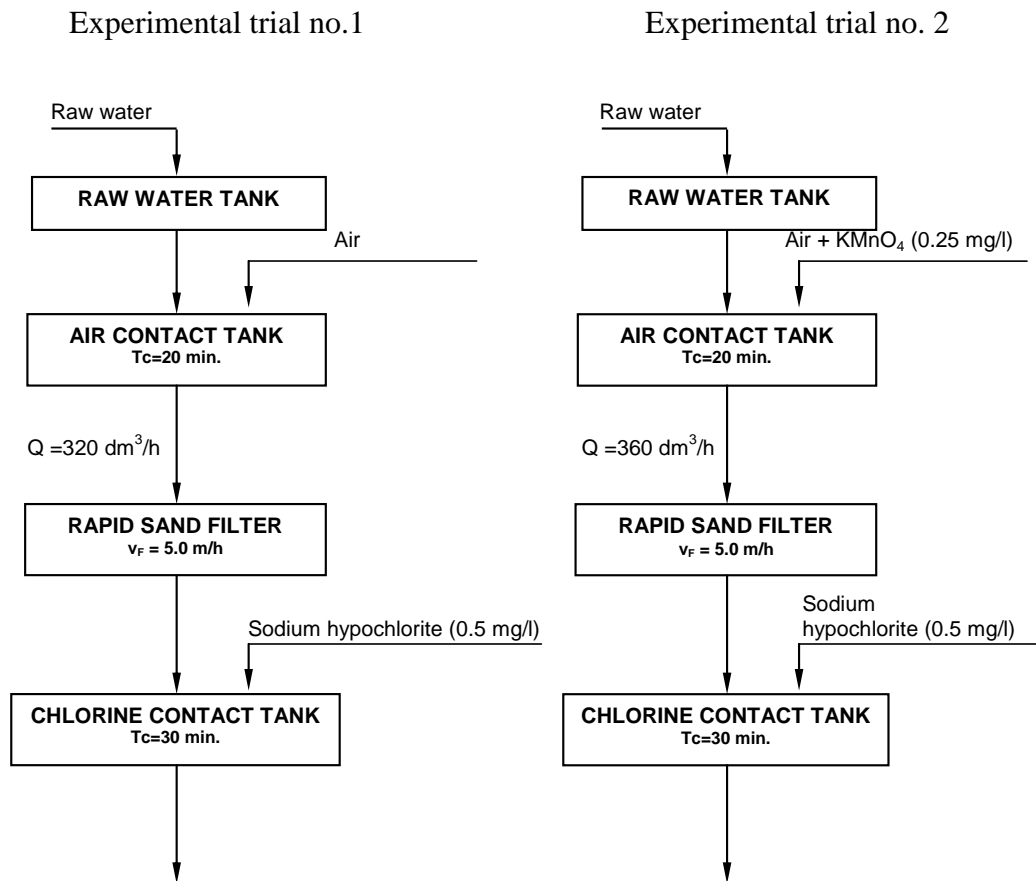


Figure 3. Technological schemes during experimental trials – Fetesti water source.

The experimental results revealed that iron concentration can be reduced up to 0.022 mg/l by air oxidation and rapid sand filtration but the concentration of manganese can be reduced only up to 0.085 mg/l which is not satisfactory, having in mind the value of 0.05 mg/l – the maximum value for drinking water according to Law 458/2002 (removal efficiency – 37.12%).

For this reason, in trial no. 2 it has been added potassium permanganate for manganese oxidation. The main reasons for using potassium permanganate are (EPA, 1999):

- Potassium permanganate is a manganese oxidation specific reagent;
- It reacts with high efficiency at high pH values;
- The use of potassium permanganate has a low potential for by-products formation;
- The manganese is totally oxidized if the reaction time is enough;
- Overdosing of potassium permanganate gives to water a pink color which is immediately observable;
- The insoluble MnO_2 can be easily retained by rapid sand filtration;
- The insoluble MnO_2 reacts as catalyst and has the ability to adsorb other ions from water (Fe^{2+} , Mn^{2+} , Ra^{2+}) increasing the removal efficiency of these ions; Also, insoluble MnO_2 has the ability to adsorb the natural organic matters from water, which represents the precursors for THM formation in disinfection process;
- The KMnO_4 doses are low: 0.94 (mg KMnO_4 / mg Fe) and 1.92 (mg KMnO_4 /mg Mn) respectively.

Fig. 4 a, b presents images during the experimental trials. It can be observed that during the experimental trial no. 2 (with potassium permanganate added), the pre-oxidized water is slightly

colored because manganese dioxide is formed.

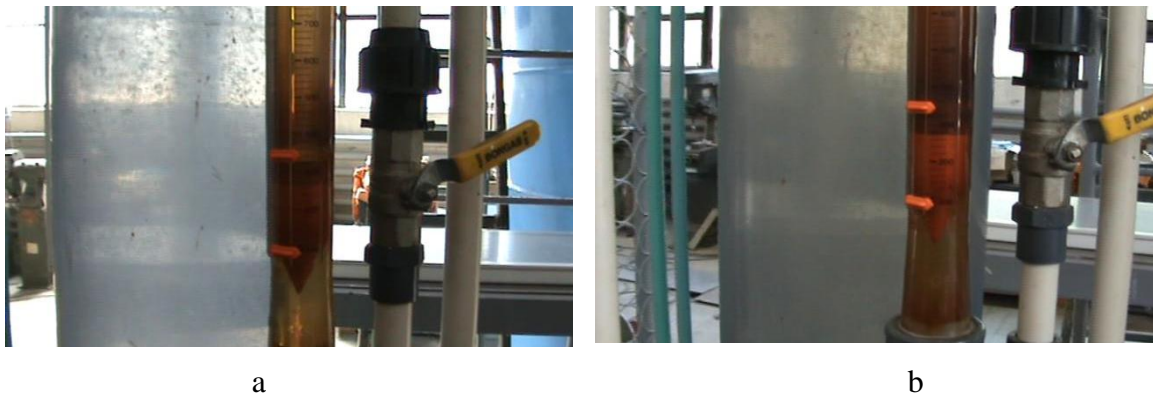


Figure 4. Pre-oxidation tank: a. trial 1 – oxidation by air; b. trial 2 – oxidation by air and potassium permanganate

Figs. 5 and 6 present the experimental results for the both experimental trials. The analysis of experimental results revealed the followings:

- the concentration of iron decreased from 0.17 mg/l for raw water to 0.01 mg/l for treated water in the case of oxidation with air and potassium permanganate (removal efficiency – 92.94%);
- the concentration of manganese decreased from 0.14 mg/l for raw water to 0.014 mg/l for treated water (removal efficiency – 90%).

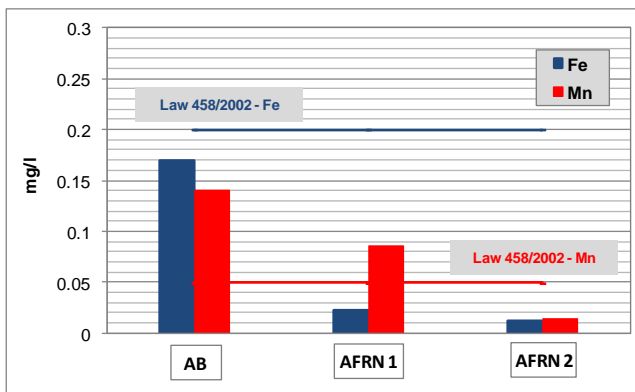


Figure 5. Variation of concentrations of iron and manganese. AB – Raw water; AFRN1 – rapid sand filtered water – trial 1; AFRN2 – rapid sand filtered water – trial 2.

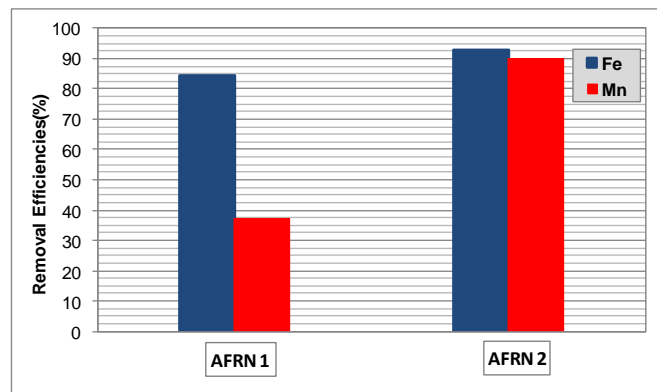


Figure 6. Variations of the removal efficiencies for iron and manganese. AFRN1 – rapid sand filtered water – trial 1; AFRN2 – rapid sand filtered water – trial 2.

The results of experimental researches revealed the fact that the removal of iron from water can be achieved by oxidation with air and rapid sand filtration up to concentrations lower than the imposed value for drinking water by enforcement legislation, while for an efficient removal of manganese it is necessary to add potassium permanganate to act as a catalyst.

3.3 Experimental trials on Tandarei water source

Because the raw water had the concentration of ammonia higher than the maximum value imposed for drinking water (0.99 mg/l towards 0.5 mg/l according to Law 458/2002) it was selected chlorine oxidation.

During the experimental trial no. 1, the technological scheme consisted of:

- pre-oxidation with sodium hypochlorite - 8.5 mg Cl₂/l (chlorine dose was determined experimentally by performing a break-point chlorination curve);
- rapid sand filtration for iron and manganese removal.

Fig. 7 presents the technological scheme during the experimental trial no. 1. The experimental results revealed the followings:

- the chlorine oxidation and rapid sand filtration determined an iron concentration of 0.01 mg/l related to 0.2 mg/l the maximum value imposed for drinking water; the removal efficiency was 97.22%. It should be noted that since the first hour of pilot plant operating, the iron concentration was 0,01 mg/l;
- the manganese was removed from 0.22 mg/l for raw water to 0.07 mg/l for treated water towards 0.05 mg/l the maximum value imposed for drinking water by Law 458/2002, which it was considered not satisfactory;
- the ammonia concentration was 0.1 mg/l in the treated water related to 0.94 mg/l for the raw water and 0.5 mg/l the maximum value imposed for drinking water.
- the free chlorine concentration was 0.19 mg/l and the total chlorine concentration was 0.31 mg/l. This revealed that the chlorine fully reacted with ammonia and the chloramines concentration was low.

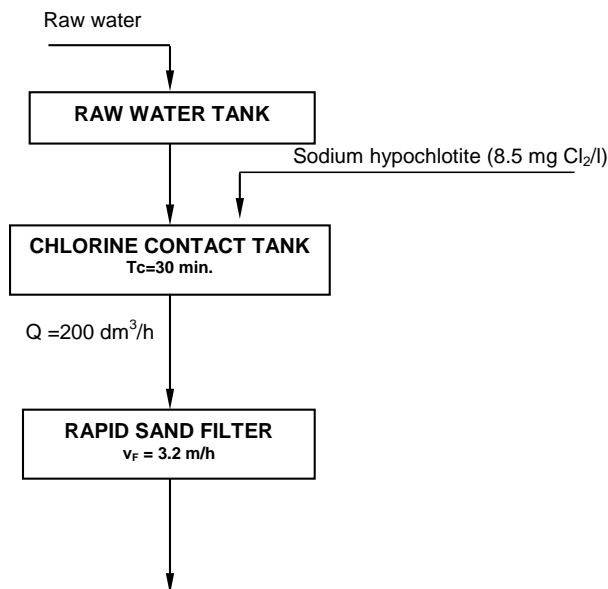


Figure 7. Technological scheme – experimental trial no.1 – Tandarei source.

Fig. 8 presents the results of experimentally determination.

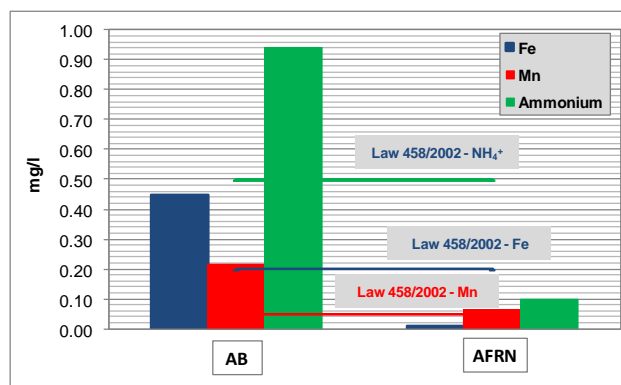


Figure 8. The variations of iron, manganese and ammonia concentrations – experimental trial no.1. AB – raw water; AFRN – rapid sand filtered water.

It can be concluded that the use of chlorine in the pre-oxidation process for removal of all three compounds does not lead to a good quality of the treated water. The determination of chlorine doses and the control of the process are difficult. Because the concentration of the manganese in treated water was higher than the maximum value imposed for drinking water, in the experimental trial no. 2 it was selected a two stages water treatment scheme:

- iron and manganese removal by oxidation with air and potassium permanganate;
- ammonia removal by break point chlorination.

The technological scheme for this experimental trial is presented in Fig.9.

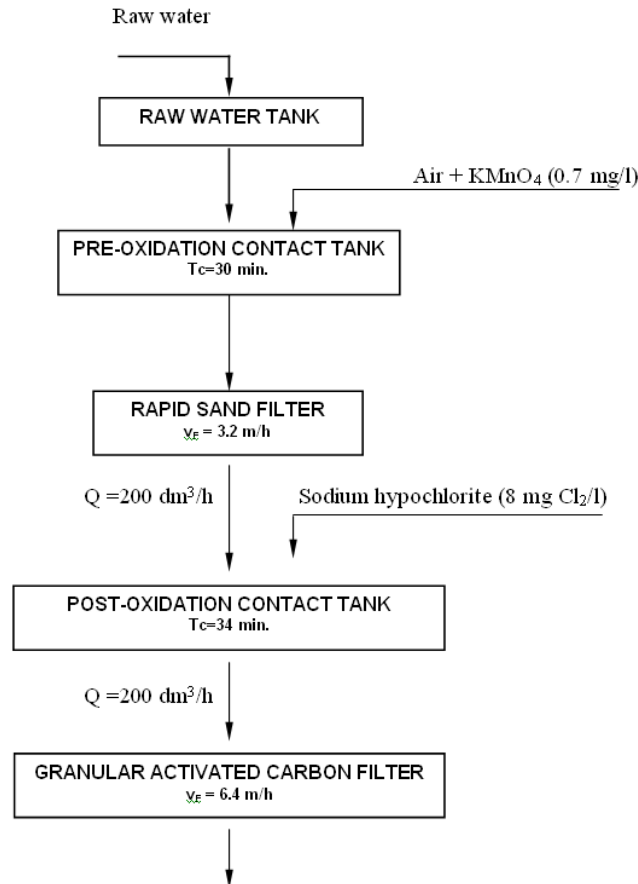


Figure 9. Technological scheme – experimental trial no. 2 – Tandarei water source.

Figs. 11 and 12 present the results of the experimental trials.

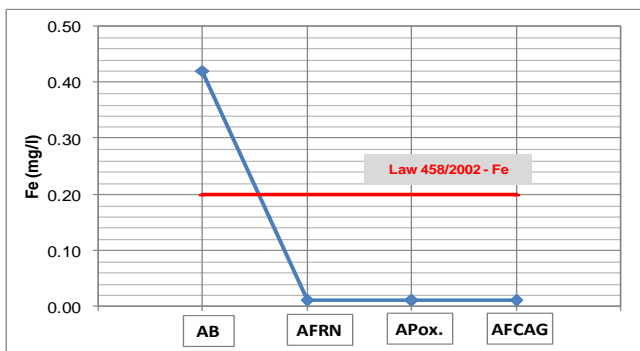


Figure 11. The variation of the iron concentration on technological scheme – trial no. 2. AB – raw water; AFRN – rapid sand filtered water; APox. – post-oxidated water; AFCAG – GAC filtrated water.

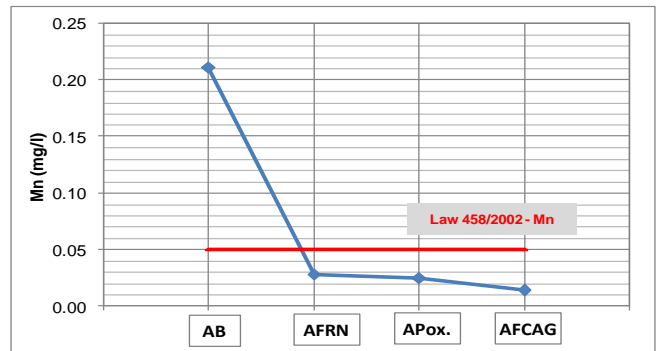


Figure 12. The variation of the manganese concentration on technological scheme – trial no. 2. AB – raw water; AFRN – rapid sand filtered water; APox. – post-oxidated water; AFCAG – GAC filtrated water.

The concentration of iron decreased from 0.42 mg/l in the raw water to 0.01 mg/l for treated water by oxidation with air and potassium permanganate and rapid sand filtration. The removal efficiency was 97.6%.

The concentration of manganese decreased from 0.211 mg/l for raw water to 0.03 mg/l for rapid sand filtered water and to 0.01 mg/l for water treated with sodium hypochlorite and granular activated carbon (GAC) filtered towards 0.05 mg/l, the maximum admissible value for drinking water.

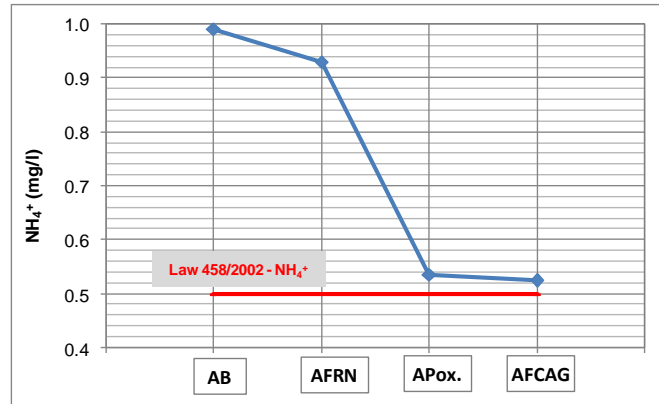


Figure 13. The variation of the ammonia on technological scheme – trial no.2. AB – raw water; AFRN – rapid sand filtered water; APox. – post-oxidated water; AFCAG – GAC filtrated water

Regarding ammonia removal, the technological scheme did not achieve a sufficient quality of the treated water. The concentration of ammonia for the post-oxidized water with sodium hypochlorite was 0.54 mg/l instead of the maximum admissible value of 0.5 mg/l (Fig.13). The GAC filtration unit was inserted to remove the eventual reaction by-products formed (chloramines).

The concentration of free chlorine for the post-oxidized water was 0.31 mg/l and the concentration of total chlorine was 0.94 mg/l. Because in the treated water exists in the same time free chlorine, ammonia but also a relatively high concentration of total chlorine it is considered that the reaction and treatment was insufficient.

The reaction time was around 30 minutes in the post-oxidation tank. From the post-oxidation tank the water was passed through the granular activated carbon filter where, the free and total chlorine were totally removed.

Fig. 14 presents the removal efficiencies of the three parameters of interest. It can be noticed that for iron and manganese the removal efficiencies were higher than 85% and the removal efficiency for ammonia registered a value of only 45%, insufficient for a good quality drinking water.

The treatment scheme of the 3rd experimental trial was the same as in the 2nd experimental trial except the reaction time in the post-oxidation contactor, which was doubled. By doubling the reaction time in post – oxidation process (experimental trial no. 3) it resulted a concentration of the ammonia in the treated water of 0.1 mg/l which is lower than 0.5 mg/l, the maximum value imposed for drinking water by Law 458/2002 (fig. 15).

The average concentration of free chlorine was 0.17 mg/l and the total chlorine 0.65 mg/l in the rapid sand filtered water and it was fully retained on granular activated filter.

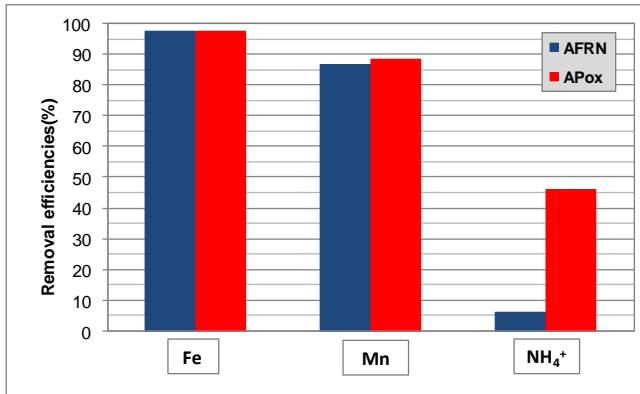


Figure 14. The removal efficiencies of interest parameters – experimental trial no.2. AFRN – rapid sand filtered water; APox. – post-oxidated water.

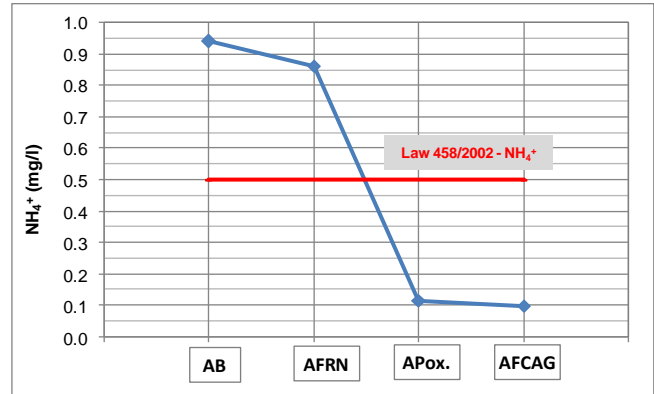


Figure 15. Variation of the ammonia concentration on technological scheme – experimental trial no.3. AB – raw water; AFRN – rapid sand filtered water; APox. – post-oxidized water; AFCAG – granular activated carbon filtered water.

4. Conclusions

The experimental researches revealed the following:

- When manganese registers high concentrations in the raw water, simple air oxidation does not respond for an efficient removal. Addition of potassium permanganate can solve the problem due to the catalytic effect;
- When the raw water contains iron, manganese and also ammonia, the treatment scheme is more complicated and as we could observe, the most important criteria for obtaining good quality drinking water are:
 - The order of the processes: iron and manganese removal come first and ammonia removal secondly;
 - Use of combined oxidative processes by air diffusion and also potassium permanganate enhance the manganese removal;
 - Break-point chlorination represents an efficient procedure for ammonia removal. Though, the high chlorine dose determines a risk related to THM formation, fact which requires an adsorption on GAC. Another important aspect is that sufficient reaction time has to be achieved, recommendable one hour.

The kinetics of the processes for iron and manganese and also of the ammonia removal are well known in the case in which one of the above mentioned products are presented in water. The problem becomes much more complicated in the case in which all products are present in the same time. The efficiency of the treatment process becomes very low if the correct order of the processes and correct treatment reagents are not respected.

The research presented in the paper brings an important contribution on establishing the correct order of the treatment processes for difficult groundwater containing high concentrations of iron, manganese together with ammonia. When iron and manganese occurs in the source together with ammonia, the most efficient order of the process is iron and manganese removal using oxidative processes enhanced by potassium permanganate catalytic effect and followed by breakpoint chlorination for ammonia oxidation and removal.

The results of the pilot plant studies have been used to implement the treatment schemes for two water supplies in Romania.

5. References

- [1] Degremont - *Water treatment handbook* – Seventh edition, ISBN 978-2-7430-0970-0, France, 2007.
- [2] Mănescu A., Sandu M., Ianculescu O. - *Alimentări cu apă*, 1994, Editura Didactică și Pedagogică, București.
- [3] Directiva 98/83/EC - *Calitatea apei destinate consumului uman*; on line la <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=DD:15:04:31998L0083:RO:PDF>
- [4] Legea 458/2002 M.O. Nr. 552/29 iulie 2002 - *Legea privind calitatea apei potabile* cu completarile si modificarile ulterioare.
- [5] EPA, (1999), *Guidance Manual Alternative Disinfectants and Oxidants*, on line la http://www.epa.gov/ogwdw/mdbp/alternative_disinfectants_guidance.pdf