Technology for treatment of groundwater simultaneously containing iron, manganese, ammonium and organic matter

Ramunė Albrektienė, Mindaugas Rimeika, Birutė Tamulaitienė and Violeta Vošniene

ABSTRACT

The groundwater used as drinking water often contains unacceptable amounts of iron and manganese compounds and ammonium ions. These substances are efficiently removed using conventional technologies (aeration and filtration through granular media filters). However, the efficiency is drastically reduced for water containing considerable amounts of organic matter, which usually enters the water in wellfields linked with surface water. This paper presents a technology development for treating groundwater with such complex problems. A combination of open and closed aeration and filtering through three filters containing sand, zeolite and sand with oxidizing bacteria are used. Polyaluminium chloride acting as coagulant is the only chemical substance used in the technology. The developed water treatment technology was tested for eight months. The technology ensured the reduction of iron, manganese, ammonium, and organic compounds by 98%, 87%, 99%, and 80%, respectively. The efficiencies are sufficient to meet the requirements of the Council Directive 98/83/EC on the quality of water intended for human consumption for most wellfields fed by both underground and surface water.

Key words | ammonium, coagulation, groundwater, iron, manganese, organic matter

INTRODUCTION

It is quite common that the groundwater from deep wells contains iron at concentrations above the quality standards for water intended for human consumption (in the EU defined as 200 μg/L by Directive 98/83/EC). The large iron concentration is often accompanied by large ammonium and manganese concentrations exceeding the standards (according to 98/83/EC, 0.5 mg/L and 50 μg/L, respectively). In drinking water treatment plants, these ions and compounds are efficiently removed by aeration and filtration through granular media filters (Yang et al. 2004; Hanbay et al. 2009; Bruins et al. 2014, 2015) or other conventional technologies.

The efficiency of the technologies are substantially decreased by pollution of the water by organic matter. At high concentrations of organic matter, the filter grains become covered by a hydrophobic film inhibiting the removal of ammonium ions and iron and manganese compounds from the water. This film is barely removed by conventional filter washing (Valentukevičienė & Rimeika 2004). Moreover, the organic compounds efficiently bind oxygen, which is necessary for oxidation of ammonium ions and iron and manganese compounds. Metals can also form complex metal–organic compounds (Munter et al. 2008). The removal of organic compounds containing iron is complicated; they are not removed using just aeration and filtration through granular media filters. Meanwhile, the organic compounds have an impact on taste and odour, which are unacceptable for water.
intended for human consumption (Shao et al. 2013). Moreover, in the process of water disinfection, the organic compounds might transform into disinfection by-products like haloacetic acid and trihalomethanes (Qu et al. 2012; Zhou et al. 2014; Bongiovani et al. 2016). Most of the compounds are pharmacologically active and exhibit properties hazardous for humans (Pavagadhi & Balasubramanian 2013).

Groundwater containing considerable concentrations of organic matter, in addition to ammonium ions and iron and manganese compounds, is treated using chemical treatment technologies. In chemical water treatment technologies, many chemicals (coagulants, oxidizing agents, acids and bases) have to be used (Potgieter et al. 2005). The treatment process becomes more complex and expensive; the operation costs are considerably higher due to the permanent consumption of chemicals, the equipment for their dosage, and addition of their delivery and storage. On the other hand, the usage of large amounts of chemicals is not acceptable for water intended to be used for human consumption. Therefore, the development of consumer-friendly methods and technologies for the efficient treatment of water simultaneously containing ammonium ions and iron and manganese compounds exceeding drinking water values and considerable amounts of organic matter is still a challenge. Separate technologies for the removal of organic compounds from surface water (Odegaard et al. 2010), iron and manganese compounds and ammonium ions (Tekerlekopoulou & Vayenas 2008), as well as complex iron organic compounds from deep groundwater (Munter et al. 2008) are well established.

The objective of this paper was to develop a technology for treatment of drinking water simultaneously containing large amounts of organic matter and high concentrations of ammonium ions and iron and manganese compounds. Fewer chemicals and higher efficiency were targeted as the key performances for developed treatment plants. The technology presented in the paper was designed to treat the water by three filtration stages adding air and the coagulant. The aim of the research was to test the technology under real conditions using industrial-made facilities for small-scale treatment plants.

**MATERIALS AND METHODS**

**Well water characterization**

The pilot plant was installed in the wellfield of Nida town in Lithuania (55°33′N21°04′E). The wellfield was selected for testing because of its location on the narrow Curonian Spit separating the Curonian Lagoon from the Baltic Sea. The Nida wellfield is a typical open-type wellfield. Quaternary rock contains the water used for the centralized water supply of Nida town. The wellfield has a thickness of 14–20 m of a groundwater aquifer composed of medium and fine grained sand. Groundwater is recharged with precipitation from the atmosphere. The main parameters of the groundwater aquifer at the wellfield of Nida are: average filtration value 9 m/d, filtration permeability value 120–180 m²/d, level permeability value $4 \times 10^3$ m²/d.

Groundwater is located within the wellfield area at a depth of 2–5 m from the surface. The quality of groundwater at the watershed of the aquifer, i.e. the dunes, is good. However, further on, as the water filtrates through limnic or marine deposits rich with organic substances it acquires a greater mineralization value and becomes contaminated with nutrients. The annually average water consumption rate from the Nida wellfield is 533 m³/d (lowest in December – 300 m³/d, highest in August – 1,100 m³/d, as the town is a popular summer resort). The wellfield water contains large concentrations of iron, manganese, ammonium, and organic matter. There are no contamination sources near this site; the water composition depends upon the marine deposits. The key characteristics of the water in this site are listed in Table 1. The pilot plant was installed near to well No. 2 of the Nida wellfield.

<table>
<thead>
<tr>
<th>Water quality indicator, units</th>
<th>Average and standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.39 ± 0.07</td>
</tr>
<tr>
<td>Permanganate index, mgO₂/L</td>
<td>6.02 ± 0.32</td>
</tr>
<tr>
<td>Total iron, μg/L</td>
<td>5,650 ± 220</td>
</tr>
<tr>
<td>Ammonium, mg/L</td>
<td>1.66 ± 0.08</td>
</tr>
<tr>
<td>Manganese, μg/L</td>
<td>252 ± 10</td>
</tr>
<tr>
<td>Colour, mgPt/L</td>
<td>34 ± 2</td>
</tr>
</tbody>
</table>
Water treatment facility

The setup of the pilot plant for drinking water treatment is presented in Figure 1. The water from the well (1) was pumped into an open aerator (3). The pilot plants were designed for a flow of 100 L/h. The aerator is an open 200 L container. Water is sprayed by a specially designed sprayer with three weirs to improve the saturation of air oxygen. Enhancing the oxidation helps to remove about 60–70% of hydrogen sulphide by aeration process (Al Haddad et al. 2014). The pump (4) delivers the water to the first filter (8) acting at a filtering rate of 2.5–3.0 m³/m²/h. Before the filter (8), polyaluminium chloride, acting as coagulant, is introduced using dosing pump (5) to maintain the coagulant concentration at 5 mgAl/L. The coagulant concentration is fixed to optimize formation of flakes of organic compounds and coagulant. Before the pilot plant, extensive jar tests were done to identify the best applicable coagulants and doses. The water with coagulant flows through a plastic pipe, 50 m long and 25 mm in diameter, acting as a reaction chamber (7), which ensures a reaction time sufficient for flake formation. The water passes through the reactor in 22 min and enters the first pressure filter (8), which is 1,200 mm high and 250 mm in diameter. The filter (8) is filled in with quartz sand, grain size fraction 1–2 mm. The filter decreases the concentrations of iron and organic compounds. After passing the filter, the water flows to a closed aerator (9), 1,100 mm high and 200 mm in diameter, which is fed with oxygen by using a compressor. The aerator (9) enriches the water with air containing oxygen, which is necessary for further oxidation of ammonium ions and manganese compounds. Then, the water enters the second pressure filter (10), 1,200 mm high and 250 mm in diameter, which contains natural zeolite (clinoptilolite) (size fraction 0.3–0.6 mm). The third pressure filter (11), 1,200 mm high and 250 mm in diameter, is filled in with quartz sand (size fraction 1–2 mm) containing oxidizing bacteria. The output of the third filter delivers clean water, which is acceptable to meet the requirements of Council Directive 98/83/EC on the quality of water intended for human consumption.

The water flow meter is installed at the inlet to the pilot plant. The pressure gauges installed before and after each filter measure the pressure drops on the filter. The pressure difference is used as an indicator to start filter washing. The filters are backwashed when either the pressure drop on the filter reaches 0.6 bar or the water quality indicators decrease below the standard limits. Filtered water is collected into 1 m³ volume containers used for backwashing at a rate of 20 m³/m²/h for 15 min.

The water treatment plant was set up in April 2012 and tested for eight months. The water samples, 1 L in volume, were extracted directly from the well and from six locations: after the open aerator, the reaction chamber, the first filter, the closed aerator, and the second and third filters. The samples were stored in cooled containers at a temperature fixed at 5°C. The samples were delivered to the testing laboratory within 24 hours. The measurement of iron, ammonium, manganese, and organic matter concentrations,
colour, pH, and amounts of dissolved oxygen and aluminium were carried out using the methods specified by the international ISO standards. The measured values presented in this paper are the averages of five measurement results with deviations below 5%.

RESULTS AND DISCUSSION

It is generally accepted that pH is very important for the removal of organic matter, ammonium ions and iron and manganese compounds from groundwater. The removal of ammonium ions, iron and manganese compounds efficiently proceeds at pH above 7.0, while an efficient removal of organic matter proceeds at pH below 7.0. In the water treatment pilot plants pH was not changed, except the pH value was influenced by the coagulant dose. The water pH was measured in the samples from all the water extraction locations in the facility. The results obtained for different sampling locations are presented in Figure 2.

The pH of groundwater in the well equals 7.39 and is not changed in the aerator. The pH value significantly decreases down to 7.02 after introduction of acid coagulant (polyaluminium chloride). At this pH value, approximately 50–60% of the organic compounds are removed. Meanwhile, the concentration of aluminium, which is introduced with the coagulant, equals 60 μg/L, well below the acceptable value specified at 200 μg/L. As the water passes the filters, the pH gradually increases and reaches the value of 7.27 after the third filter. Meanwhile, pH values above 7.5 are required for efficient oxidation of manganese compounds. The key characteristics of the water in all steps at the water treatment plant are listed in Table 2.

The second important indicator for the processes in water treatment technologies is the concentration of oxygen dissolved in the water. The oxygen concentrations at different sampling locations in the facility are presented in Figure 3.

The groundwater contains a low amount of dissolved oxygen (0.25 mgO₂/L). The open aeration increases the oxygen concentration up to 6.03 mgO₂/L. This concentration is sufficient for efficient oxidation of soluble iron compounds. The decrease in oxygen concentration down to 3.42 mgO₂/L after the first filter is evidence of the consumption of oxygen for oxidation of iron and organic compounds. The closed aerator by blowing air increases the oxygen concentration to 7.19 mgO₂/L. The second filter decreases the oxygen content, but just to the value of 5.02 mgO₂/L, which is still sufficient for nitrification of

**Table 2 | Water quality data at different sampling locations**

<table>
<thead>
<tr>
<th>Water quality indicator, unit</th>
<th>Groundwater</th>
<th>After open aerator</th>
<th>After reaction chamber</th>
<th>After I filter</th>
<th>After closed aerator</th>
<th>After II filter</th>
<th>After III filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.39</td>
<td>7.38</td>
<td>7.02</td>
<td>7.13</td>
<td>7.15</td>
<td>7.21</td>
<td>7.27</td>
</tr>
<tr>
<td>Oxygen, mgO₂/L</td>
<td>0.25</td>
<td>6.03</td>
<td>6.05</td>
<td>3.42</td>
<td>7.19</td>
<td>5.02</td>
<td>2.29</td>
</tr>
<tr>
<td>Permanganate index (PI), mgO₂/L</td>
<td>6.00</td>
<td>6.00</td>
<td>4.20</td>
<td>1.50</td>
<td>1.40</td>
<td>1.20</td>
<td>1.15</td>
</tr>
<tr>
<td>Total iron, μg/L</td>
<td>5,625</td>
<td>4,520</td>
<td>4,392</td>
<td>2,040</td>
<td>1,950</td>
<td>859</td>
<td>111</td>
</tr>
<tr>
<td>Ammonium, mg/L</td>
<td>1.66</td>
<td>1.65</td>
<td>1.59</td>
<td>1.48</td>
<td>1.44</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Manganese, μg/L</td>
<td>252</td>
<td>250</td>
<td>248</td>
<td>220</td>
<td>215</td>
<td>212</td>
<td>33</td>
</tr>
<tr>
<td>Colour, mgPt/L</td>
<td>34</td>
<td>34</td>
<td>31</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>
ammonium ions and oxidation of manganese compounds. The considerable decrease of the oxygen concentration down to 2.29 mgO₂/L is evidence of the efficient oxidation of pollutants. Oxygen concentrations after all filters drops more than the theoretical values calculated according to the stochastic calculations. Bacteria growth occurs at all the filters’ media, as no disinfection matter was used for the treatment processes. It is still not clear how much oxygen is used for biological growth on a filter media.

The first stages of the water treatment plant are designed to remove organic compounds and reduce the water colour. The dynamics of the permanganate index reflecting the amount of organic matter and the water colour at different treatment stages are presented in Figures 4 and 5.

The permanganate index of the groundwater in the well is above the value corresponding to the water quality standard 98/83/EC (5.0 mgO₂/L). The index is decreased by coagulation. The dose of coagulant at 5 mgAl/L ensures a decrease of the index after passing the first filter by 81%, already well below the acceptable limit. The permanganate index is actually not changed in the following stages of the treatment. Thus, the facility design and coagulant dosage ensured approximately 80% efficiency of the organic matter removal via coagulation. Removal efficiency of organic matter using coagulation was slightly better than that obtained by Wang et al. (2002). The permanganate index was reduced just after the reaction chamber, as some sediment occurred in the chamber itself, and some of the easily biodegradable matter after coagulation became part of more stable units which could not be evaluated by the oxidizing material used for the PI. Deposit from the reaction chamber was washed away every 2 weeks.

The coagulation process also diminishes the water colour by 79% after the first filter. As seen in Figure 5, the treatment in the further stages has no significant effect on water colour.

The efficient removal of organic matter in the first treatment stages enables the removal of iron compounds. The dynamics of the total concentration of iron compounds after passing through different treatment stages is illustrated in Figure 6.

The total iron compound concentration in the well exceeded the water quality standard 98/83/EC. The open aerator decreased the iron amount by 20%. As evidenced by analysis of precipitates in the aerator, which were periodically removed every month, this decrease was caused by oxidation of a part of bivalent iron ions to a trivalent state and hydrolysis to trivalent iron hydroxides, which are insoluble and fall as precipitates. However, the part of the iron ions oxidized at this stage is quite small. The research of
Setyadhi & Liu (2013) shows that the iron removal is more complicated if humic acid exists, or iron incorporated into organic compounds (Munter et al. 2008). The first filter reduced the iron concentration in the treated water containing coagulant at 5 mgAl/L by 63%, while the iron concentration decreased by 85% from the initial value after the second filter containing zeolite. Iron concentration was reduced by 57% by the second filter. Vistuba et al. (2014) determined that iron concentration could be removed by 74% using zeolite. A substantial decrease in iron content in the water was achieved in the third filter containing sand with oxidizing bacteria. The total iron removal efficiency was 98%.

Results show that the combination of coagulation and filtering through sand filter enables removal of both organic matter and complex organic iron compounds. If the iron organic compounds were not removed, the next two filters would not be able to remove the compounds, and the total iron concentration could not be reduced sufficiently to reach the water quality standard. On the other hand, the efficient removal of organic iron compounds in the first filter does not ensure the acceptable level of the total iron concentration. Two subsequent filters in the system are necessary for substantial removal of inorganic iron compounds.

As shown in Figure 7, the concentration of ammonium ions in the well also significantly exceeds the water quality standard. The ammonium ions can be efficiently removed only from water with low iron content. In the pilot plant, the ammonium was removed in the second filter containing zeolite. Zeolite removed the ammonium ions from water via adsorption. The adsorption ability of zeolite weakens with time of filter operation but the zeolite can be regenerated by a solution of sodium chloride.

As is evident in Figure 7, the ammonium concentration is approximately constant until the second filter. This observation confirms the assumption that ammonium ions do not participate in formation of complex organic compounds. Otherwise, the ammonium concentration would drop after the first filter, where the flakes formed by coagulation and containing the complex organic compounds are removed. Instead, the ammonium concentration decreased only after the second filter containing zeolite. Our results confirm the results of other researchers (Langwaldt 2008; Mazeikiene et al. 2008) that zeolite efficiently removes ammonium ions from water.

Natural origin zeolite (clinoptilolite) (0.3–0.6 mm), Clinobrite®, was used. Zeolite was replaced every two months, but only twice as the last four months’ zeolite media was not changed and let oxidizing bacteria grow. Thus, in the last two months of treatment the zeolite adsorption capacity was completely exhausted, but ammonium removal efficiency was at the same level. Thus, it can be proved that ammonium was decreased by oxidation in the second filter. Ammonium oxidizing bacteria grew for one to two months, but later biological processes were able to remove ammonium if concentration was below 1.5 mg/l. Ammonium removal efficiency was rather stable at all research periods. At the first week ammonium was removed mostly by adsorption, but simultaneously oxidizing bacteria was growing. After two months ammonium was removed mostly by biological processes. This process was repeated twice, with the same results. After ammonium ions are
ammonium ions simultaneously with a large content of organic matter was developed, the water treatment plant was fabricated and installed at the wellfield, and was tested for eight months of operation. The treatment technology consisted of three stages of filtration with open and closed aeration and coagulation. The choice of the sequence of treatment stages and the optimization of treatment conditions at every stage enabled high treatment efficiency with minimal use of chemicals. In the entire treatment process, only one chemical (polyaluminium chloride acting as coagulant) was used. The testing results, which were obtained by treating water, show that the efficiencies of removal of all the components meet the requirements specified in the Council Directive 98/83/EC. The technology ensures the reduction of iron, manganese, and ammonium content by 98%, 87%, and 99%, respectively, and decreases the concentration of organic compounds and water colour by 80%. The developed technology is recommended for operation in wellfields fed by groundwater with large contents of iron, manganese and ammonium and containing considerable amounts of organic matter.

REFERENCES


removed in the second filter, the third filter serves for removal of manganese compounds. The filter contains sand with oxidizing bacteria. The change in the concentrations of manganese during the stages in the water treatment facility are presented in Figure 8.

The first filter decreases the manganese concentration only by 13%. This is expected, since the water at this stage contains large amounts of iron compounds and ammonium ions, pH is too low for efficient oxidation of manganese compounds, and the filter does not contain oxidizing bacteria to enhance the oxidation. Similar results were presented by Leal et al. (2015), where manganese removal by coagulation was not effective. As observed in testing different filter fillings carried out before designing the treatment facility, zeolite does not remove manganese compounds. Vistuba et al. (2014) conducted research that found zeolite reduction of manganese by 66%. However, Skoczko et al. (2015) determined that zeolite is not useful for manganese removal. Thus, the second filter does not affect the manganese content. The content is substantially decreased below the limit of the water quality standards in the third filter containing sand with oxidizing bacteria. The obtained results were confirmed by Yang et al. (2004) that manganese is removed effectively using filters with oxidizing bacteria.

CONCLUSIONS

Technology for treatment water containing large concentrations of iron and manganese compounds and

![Manganese concentrations at different sampling locations. Horizontal line indicates the value corresponding to the water quality standard 98/83/EC.](image-url)


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