Ion-exchange demanganation of drinking waters in the Oktyabrsky District of the Jewish Autonomous Region

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Abstract. The aim of the study is the analysis of the possible use of ion-exchange demanganization of drinking water in the Oktyabrsky District of the Jewish Autonomous Region to reduce the concentration of manganese to a value below MPC. For the ion-exchange demanganization of drinking water, a domestically-produced KU-2-8 ES cation exchanger and an imported Purolit C120 E cation exchanger were used as adsorbents. We used four different methods, reproducing purification with drinking filters in domestic conditions. We have determined that among 33 analyzed water samples, 16 of them, which were combined into groups No. 2 and No. 4, exceeded the MPC value for gross manganese. This fact indicates that these waters require treatment and conditioning for drinking purposes. We have revealed the ranges of concentrations for indicators of the physiological relevance of water: the total hardness is 1.5–7 meq / dm³, the calcium content is 25–130 mg / dm³, and the magnesium content is 5–65 mg / dm³. This fact indicates that the concentrations of calcium and magnesium, as well as the total hardness in the water, are below the lower limits of their physiologically relevant concentrations in drinking water.

1. Introduction

It is well known that when a person consumes drinking water with manganese (Mn) content higher than the normal maximum permissible concentration (MPC) of 0.1 mg/dm³ [1], various diseases, such as musculoskeletal and nervous system-related problems, can develop. With a long-term residence of a person in a territory with high Mn in the soil and water, more serious central nervous system-related pathologies and dysfunctions can be observed. Mn enters the human body not only in the drinking water but also through the diet. An adequate level of average daily Mn intake for an adult is approximately 2 mg, and an allowable upper level of consumption is approximately 11 mg. If high concentrations of Mn are detected in drinking water, the next task will be the development and application of water conditioning methods to bring the water to required Mn levels safe to the health.

Water supply (up to 99%) to the settlements of the Jewish Autonomous Region is obtained mainly as groundwater. These waters are located at a shallow depth of approximately 10 to 15 m from the upper horizon. In rural areas, individual and central wells are widely used, and decentralized individual water supply is organized for approximately 50% of the region’s population [2]. The population of the Jewish Autonomous Region widely uses the waters of the Middle Amur Artesian Basin as a source of drinking water, which is characterized by a high Mn content (sometimes reaching up to 6.2 mg/dm³) [3], high iron content [4, 5], and a deficiency of calcium and magnesium [6].
According to the state report, “On the state of the sanitary and epidemiological well-being of the population in the Jewish Autonomous Region”, manganese is one of the priority indicators of chemical pollution of drinking water in the region, and the Oktyabrsky Municipal District is included in the list of districts with the worst iron- and manganese-related drinking water pollution [7].

In 2017, 18.8% of the samples of drinking water from the centralized water supply exceeded the hygiene standard for manganese. It can be assumed that the proportion of drinking water samples from a non-centralized water supply, which exceeded the hygienic standard for manganese and did not undergo demanganization, was several times higher. In addition, the composition of the drinking water in this region is affected by periodic floods, including flooding of significant residential areas, which leads to deterioration in the ecological state of the surface and underground waters as well as soil cover [8].

The study aims to analyze the possible use of ion-exchange demanganization of drinking water in the Oktyabrsky District of the Jewish Autonomous Region to reduce the concentration of manganese to a value below MPC.

The Oktyabrsky Municipal District is located in the southern part of the Jewish Autonomous Region on the left bank of the Amur River and has an area of approximately 6.4 thousand km². It includes three large rural settlements (Amurzet, Nagibovo and Polevoe) and 15 less-populated villages with a total population of 9708 people (2018).

Within the district’s territory, there is the South Khingan manganese-iron ore deposit (12 km north of the village of Stolbovoye). The manganese balance reserves are (in terms of ore) oxidized, with an average content of 18.1%, categories A + B + C1 of approximately 127 thousand tons; mixed, with an average content of 20.9%, categories A + B + C1 of approximately 6004 thousand tons; categories C1 of approximately 285 thousand tons; and oxide, with an average content of 21.1%, categories A + B + C1 of approximately 285 thousand tons; categories C2 of approximately 381 thousand tons. The predicted resources of the South Khingan ore field are 25 million tons of ore [9]. It is the presence of iron-manganese ore deposits in the region that most likely explains the increased concentration of gross manganese in the ground and under-bed waters of the rivers, which the locals use for drinking purposes.

2. Models and methods

For the ion-exchange demanganization of drinking water in the Oktyabrsky District, a domestically-produced KU-2-8 ES cation exchanger and an imported Purolit C120 E cation exchanger were used as adsorbents. In the laboratory, ion-exchange demanganization was carried out using four different methods to reproduce its purification with drinking filters under domestic conditions. The first demanganization method was the purification of drinking water with a household jug filter cartridge or a special filter nozzle placed directly on a tap water mixer (through KU-2-8 emergency cation exchange resin and coconut coal KAU-A). The second method simulated water purification with a removable cartridge for household filtration systems “under the sink,” with a large amount of filtering backfill compared to filtering jugs (through KU-2-8 emergency cation exchange resin). The third method was similar to the second but included a 1000-cm³ separatory funnel with activated coconut carbon KAU-A as a preliminary sorption filter. The fourth method was similar to the first, but an imported Purolit C120 E cation exchange resin was used as the ion-exchange resin.

The material for the work was the analysis of 33 drinking water samples from centralized and non-centralized water supply sources of the Oktyabrsky District from December 01, 2018 to March 31, 2019. The samples were evaluated according to four controlled indicators: total hardness, the mass concentration of calcium, magnesium ions, and total content of all forms of manganese (132 definition elements).

To determine the total manganese content in the water samples (gross manganese), we used the photometric method with formaldoxime according to the guiding document of the Federal Service for Hydrometeorology and Environmental Monitoring RD 52.24.467-2008 [10].
The total hardness in samples was determined by the titrimetric method according to the environmental regulatory document PND F 14.1: 1997. The titrimetric method is based on titration of a sample with a solution of Trilon B, which is a disodium salt of ethylenediaminetetraacetic acid. Titration was carried out in the presence of an eriochrome black indicator [11].

The mass concentration of Ca²⁺ ions was determined by the titrimetric method according to PND document F 14.1: 1997. This method is based on the Ca²⁺ ion’s ability to form a complex compound with Trilon B. The titration endpoint was determined by color change using murexide as an indicator [12].

The mass concentration of Mg²⁺ ions was calculated from the difference in the amounts of Trilon B titrant used for the titration of the sum of the Ca²⁺ and Mg²⁺ ions and Ca²⁺ ions separately in equal sample volumes [13].

3. Results and discussion

Table 1 shows the results of the initial analysis of the drinking water as follows: Xav ± ∆, with probability P = 0.95, where Xav is the arithmetic mean of the results of parallel determinations and ∆ is the accuracy indicator of the technique. Here, ∆ = 0.01 · δ · Xav, where δ is the accuracy indicator (the boundaries of the relative error with probability P = 0.95) (table 1).

| Sample group | Concentration, | Total rigidity mEq / dm³ |
|--------------|----------------|-------------------------|
|              | Mn, mg / dm³ | Ca, mg / dm³ | Mg, mg / dm³ |                       |
| Water from non-centralized water supply sources. | | | | |
| First one, C_Mn<0.1 mg / dm³ | 14 | 0.08±0.01 | 25.21±2.12 | 5.18±0.42 | 1.52±0.08 |
| Second, C_Mn>0.1 mg / dm³ | 4 | 0.21±0.02 | 28.21±2.89 | 5.66±0.55 | 1.64±0.09 |
| Water from non-centralized water supply sources. | | | | |
| Third, C_Mn<0.1 mg / dm³ | 3 | 0.08±0.01 | 43.26±5.02 | 13.46±1.55 | 2.66±0.31 |
| Fourth, C_Mn>0.1 mg / dm³ | 12 | 0.34±0.03 | 49.58±5.17 | 15.25±1.76 | 2.98±0.28 |

According to the controlled indicators, 16 water samples were also analyzed with an initial concentration of gross manganese higher than the MPC standard C ((Mn) = 0.1 mg / dm³) after their demanganization on strongly acidic KU-2-8 ES and Purolit C120 E cation exchangers (64 definition elements) (table 2).

As a metal, manganese is polyvalent; therefore, in natural waters, it can be present in various oxidation degrees, i.e. Mn²⁺, Mn³⁺ or Mn⁴⁺. Manganese dioxide (MnO₂) is sparingly soluble but highly stable in natural waters. Therefore, the suspended forms of manganese are predominant in comparison with others. Manganese compounds with higher oxidation states, such as 6⁺ or 7⁺, are unstable in the aquatic environment and, as a rule, not found in natural waters.
Table 2. Selected indicators of the quality of drinking water in the Oktyabrsky District after ion exchange demanganization, n-number of samples.

| Sample Group | n | Mn, mg / dm³ | Ca, mg / dm³ | Mg, mg / dm³ | Total rigidity mEq / dm³ |
|--------------|---|--------------|--------------|--------------|------------------------|
| 1st method   |   |              |              |              |                        |
| Second       | 4 | 0.05±0.01    | 12.11±1.14   | 3.16±0.38    | 0.44±0.06              |
| Fourth       | 2 | 0.07±0.01    | 23.15±2.16   | 4.48±0.88    | 1.44±0.12              |
| 2nd method   |   |              |              |              |                        |
| Second       | 4 | 0.06±0.01    | 14.14±1.78   | 3.28±0.42    | 0.52±0.08              |
| Fourth       | 2 | 0.08±0.01    | 24.92±2.55   | 4.11±0.92    | 1.48±0.15              |
| 3rd method   |   |              |              |              |                        |
| Second       | 4 | 0.05±0.01    | 12.38±1.22   | 3.12±0.34    | 0.48±0.06              |
| Fourth       | 2 | 0.07±0.01    | 23.26±2.34   | 4.22±0.82    | 1.34±0.14              |
| 4th method   |   |              |              |              |                        |
| Second       | 4 | 0.03±0.01    | 11.10±1.02   | 3.02±0.30    | 0.34±0.05              |
| Fourth       | 2 | 0.04±0.01    | 21.53±2.86   | 3.54±0.72    | 1.32±0.11              |

Quantitative chemical analysis of drinking water samples was carried out before and after their purification on ion-exchange resins and sorbents. Moreover, purification with cation exchangers was carried out only for those water samples, in which a high concentration of gross manganese was previously established according to the SanPiN 2.1.4.1074-01 C (Mn) = 0.1 mg / dm³ standard [1]. Notably, the hygiene requirements for the water quality of non-centralized water supply sources are reflected in SanPiN 2.1.4.1175-02; however, the specified normative document does not provide the MPC standard for total manganese but does give instructions for its implementation. Therefore, the standard for gross manganese for water from non-centralized sources in this study was also taken as 0.1 mg / dm³ according to SanPiN 2.1.4.1074-01.

4. Conclusion

Thus, among 33 water samples analyzed, 16 of them, which were combined into groups 2 and 4, exceeded the MPC value for gross manganese of more than 0.1 mg / dm³. This fact indicates that these waters require cleaning and conditioning for drinking purposes. After purification through cation exchangers and sorbents, the sample indices were redefined. As a result, in all the analyzed water samples, the manganese content was lower than the MPC value, which confirms the effectiveness of this method of demanganization.

Our study shows that this cleaning method significantly reduces the concentrations of calcium and magnesium, which are important and necessary nutrients for the human body. Moreover, such cleaning decreases the content of calcium and magnesium as well as the level of general hardness to values below their physiologically relevant concentrations in drinking water. Therefore, the widespread use of drinking filters in everyday life can lead to a decrease in the concentrations of extremely important nutrients in drinking water.

In the territory of the Oktyabrsky District, we have determined the following ranges of concentrations for the indicators of the physiological relevance of water: the total hardness is 1.5–7 mEq / dm³, calcium content is 25–130 mg / dm³, and magnesium content is 5–65 mg / dm³. This fact indicates the concentrations of calcium and magnesium, as well as the value of the total hardness in the water, are below the lower limits of their physiologically relevant concentrations in drinking water.
according to existing standards adopted in Russia. Deviations from these boundaries (increases or decreases) are deviations from the physiological norm [14].

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