Using Kuzbass underground waters for soft drinks production

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Abstract. Providing the population with drinking water and water-based quality products is Russia’s priority task, aiming at health preservation and improvement of citizens' living conditions. In addition to surface water, underground sources are used for drinking water supply. Manganese (II) can be found in a number of underground sources of the Russian Federation, including Kuzbass. We studied the effect of manganese present in groundwater on the ingredient (flavonoids, vitamin C) persistence of nectars and carbonated drinks (sucrose, citric acid, sodium benzoate, synthetic dyes). The studies were carried out in Kuzbass using titrimetric analysis, methods of molecular absorption spectroscopy and refractometry. We found a decrease in concentrations of all the key ingredients of non-alcoholic carbonated drinks and nectars in presence of manganese (II). Concentrations of sucrose remained unchanged. We explained the interaction of the ingredients of non-alcoholic carbonated drinks and nectars with manganese (II): the latter has a significant effect on their persistence, which reduces the quality characteristics of beverages during production and storage.

1. Introduction

Today water supply in Russia is one of the priority tasks, aiming at health preservation of the population and improving citizens' standard of living. The “Water Strategy of the Russian Federation” states that every second citizen of Russia drinks water which does not meet the standards. The main cause of poor drinking water quality is pollution of natural waters by technogenic impurities. Existing water treatment technologies do not allow obtaining quality water, and they require additional material costs. Therefore, groundwater can be used as an alternative source of water supply and food production. This is even more relevant for areas remote from water sources, where small enterprises for soft drinks production are usually located.

In Kuzbass, groundwater is widely used in production of food products (soft carbonated drinks, nectars, milk, baby food, etc.) [1,2]. Among other heavy metals, manganese (II) prevails: its compounds are found as water soluble Mn(HCO$_3$)$_2$ in 0.1-2 0.98 mg/dm$^3$ concentration.

The structure and properties of the ingredients and manganese (II) predetermine the interaction. In this regard, studies aimed at determining the effect of manganese on the quality of beverages are relevant. Our aim is to study the effect of manganese salts on the persistence of the ingredients, including those of plant origin, in soft drinks production and storage.
2. Materials and Methods
The study objects were aqueous solutions of sucrose, citric acid, sodium benzoate, and dyes – brilliant blue (E133), carmoisine (E122), sunset yellow (E110), ponseau 4R (E 124), green apple, as well as nectars of shadberries, cherries, honeysuckle and apple fruits, and the above mentioned objects of study with the addition of manganese (II) salts.

The concentration of sucrose was 342.3 mg/kg, citric acid was 5 mg/dm$^3$ according to CU TR 023/2011. Concentration of sodium benzoate in the samples was 0.1441 mg/dm$^3$, concentrations of dyes (brilliant blue, green apple, sunset yellow, carmoisine, ponseau) was 100 mg/kg according to CU TR 029/2012. The concentration of manganese salts in the solutions was 10 LOC, which corresponded to the possible content of the heavy metal in groundwater.

Sodium benzoate content was determined using molecular absorption spectroscopy at a wavelength of 315 nm [3]. The intensity of coloring of the dyes and nectars was also analyzed by molecular absorption spectroscopy at a wavelength of 400-440 nm. The citric acid content was determined by photocolorimetrically at a wavelength of 440 nm according to 28467-90 State Standard. Sucrose content in the samples was carried out by refractometry according to 15113.6-77 State Standard. Vitamin C found in nectars was analyzed by iodometry using indirect titration. Manganese content was analyzed colorimetrically at a wavelength of 530 nm according to 4974-2014 State Standard. Monitoring of all indicators’ changes was done within 21 days.

3. Results
Sodium benzoate is the main ingredient of non-alcoholic carbonated beverages. Its concentrations in beverages are strictly controlled by regulatory and technical documentation. We studied the persistence of sodium benzoate in presence of manganese over time (Figure 1).

**Figure 1.** Persistence of sodium benzoate in presence of manganese in water (2) and without manganese (1) over time.

Sucrose ($C_{12}H_{22}O_{11}$) is the main ingredient of carbonated beverages and nectars. Decrease in sucrose content in presence of manganese has not been found.

Citric acid ($C_6H_8O_7 \cdot H_2O$) is used in the production of non-alcoholic drinks and nectars as an acidity regulator. Experimental data on citric acid persistence in presence of manganese (II) are shown in Table 1.
Table 1. Persistence of citric acid in aqueous solution during storage, %

| Days | Citric acid, % | Citric acid in presence of manganese, % |
|------|---------------|----------------------------------------|
| 1    | 100           | 45                                     |
| 4    | 100           | 39                                     |
| 6    | 100           | 39                                     |
| 8    | 100           | 38                                     |
| 12   | 100           | 38                                     |
| 16   | 100           | 38                                     |
| 21   | 100           | 38                                     |

Dyes are widely used for coloring of non-alcoholic carbonated drinks: “Tarragon”, “Cherry aroma”, “Peach” “Green apple”, etc. We studied the color intensity of brilliant blue, carmoisin, sunset yellow, poneau, green apple dyes in presence of manganese (II) (Figure 2).

Figure 2. Color intensity of poneau (2), sunset yellow (3), brilliant blue (4), and green apple (5) in aqueous solutions with manganese and without manganese (1) over time.

Dye substances. Flavonoids provide violet and red color of fruits and berries used in the production of nectars. We analyzed the color change in nectars in presence of manganese over time (Figure 3).

Figure 3. Color intensity in apple nectars (2), honeysuckle (3), cherry (4), and shadberry (5) with and without manganese (1) over time.
Vitamins contained in nectars are organic compounds of different chemical nature. The interaction of vitamins and manganese (II) salts was studied by the example of ascorbic acid (Figure 4).

![Figure 4. Vitamin C content in cherries (2), shadberry (3), apple (4), honeysuckle (5) with manganese and without manganese (1) over time.](image)

4. Discussion of results
Decrease in sodium benzoate content (Figure 1) due to its chemical interaction with manganese (II) contained in water was found. Mn$^{2+}$ ions form coordination bonds of predominantly covalent character with sodium benzoate (Figure 5). The chemical interaction of manganese with sodium benzoate is also experimentally confirmed by a corresponding decrease in manganese in water over time.

![Figure 5. Chemical interaction of manganese (II) with sodium benzoate.](image)

A decrease in the concentration of citric acid in presence of manganese (II) was found (Table 1) due to the chemical reaction (Figure 6). The chemical interaction of manganese (II) with citric acid with the formation of complex compounds is experimentally confirmed by the complete absence of the metal in presence of citric acid in water, which is consistent with data in Table 1.

![Figure 6. Chemical interaction of manganese (II) with citric acid.](image)

In the study of the dyes' color intensity, it was found that the intensity of the samples containing sunset yellow, green apple, brilliant blue, ponceau dyes decreased (Fig. 2), which might be associated with formation of low-soluble complex compounds between dyes and the heavy metal due to ionic and
donor-acceptance bonds, which is confirmed by equations of the reactions (Figures 7-10). The carmoisine dye sample has not changed the color for the entire study period.

Figure 7. Chemical interaction of manganese (II) with sunset yellow dye in aqueous solution.

Figure 8. Chemical interaction of manganese (II) with ponseau dye in aqueous solution.

Figure 9. Chemical interaction of manganese (II) with brilliant blue dye in aqueous solution.

Figure 10. Chemical interaction of manganese (II) with green apple dye in aqueous solution.

The change in color in nectars in presence of manganese over time is caused by the formation of complexes between anthocyanins and manganese (II) in water. The greatest decrease in color is observed in presence of manganese in honeysuckle and cherry nectar (Figure 3). The chemical properties of coloring substances and the heavy metal might have predetermined their interaction (Fig. 11).

Figure 11. Chemical interaction of manganese (II) with flavonoids.
The decrease in vitamin C content in apple nectars, honeysuckle, shadberries, cherries in presence of manganese in the samples is shown (Figure 4). The reaction of complex formation between manganese (II) and ascorbic acid is shown in Figure 12. Chemical interaction of ascorbic acid and manganese salt is also experimentally confirmed by a corresponding decrease in manganese in water over time.

**Figure 12.** Chemical interaction of manganese (II) with vitamin C.

5. Conclusion
The study showed that the presence of manganese (II) salts in water has a significant effect on the persistence of the main ingredients of soft drinks (sodium benzoate, citric acids, and dyes), as well as the intensity of coloring and vitamin C preservation, which is confirmed by chemical reactions. The quality of drinks and the shelf-life reduce. Therefore, the water used for the production of soft carbonated drinks and nectars must be preliminarily treated to remove heavy metals. Adsorption treatment can be the most environmentally friendly and economical method of removing manganese (II) from groundwater [4].

References
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