Studying the Impact of Heavy Metals on the Composition of the Food and Processing Industry Wastewater in the Republic of North Ossetia-Alania

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Abstract. The intensive development of industry, the growth of cities and other settlements, and their improvement require solving the issue of preventing the negative impact of human activities on the environment. This particularly concerns the food and processing sectors, which are among the strategic pillars designed to ensure a sustainable provision of the population with the high-quality food required. Water resources rank first by the intensity of the negative impact of food and processing industry on the environment. To eliminate or reduce the damage caused to the environment by industrial waste emissions, it is proposed to switch them to closed cycles. This would allow not only solving the environmental protection issue but also rationally using natural resources. Wastewater contains feed residues, cooking salt, detergents, nitrites, phosphates, alkalis, acids, and possibly, pathogenic microflora. The paper describes a rational technology developed for the neutralization and deep purification of agricultural wastewater.

1. Introduction
The renewed growth of domestic industry and the emergence of an environment for investment in its various sectors create the preconditions for retrofitting the production and improving its control system on an advanced technical basis, considering the current requirements for environmental protection and product quality standards, and an increase in its competitiveness in international markets.

The water supply and sewerage, non-ferrous metallurgy, processing industry, and other facilities are remaining to be the main pollutants of surface water bodies in the Republic of North Ossetia-Alania. According to the Ministry of Natural Resources and Ecology of the Republic of North-Ossetia-Alania, over the past year, the number of enterprises discharging wastewater into surface water bodies has reached 31. The volume of discharges into surface water bodies amounted to 131.04 mln. m³. 94.73 mln. m³ of the total volume of wastewater discharged was polluted, which was 6.34 % more than in the previous year, of which 2.77 and 89.4 mln. m³ was non-treated and under-treated, respectively [1].
Monitoring of the Republic’s water bodies has shown that the chemical composition of the Terek River basin is formed under the impact of wastewater discharged by municipal facilities, the activity of the processing industry enterprises, and the surface and storm runoffs.

The monitoring stations below Vladikavkaz are remaining the most problematic sections of the Terek River. Despite the decrease in the pollution with organic and biogenic substances, in these sections, their level is always elevated. The average level of pollution with organic substances varies within 12.5 to 25.1 MPC, respectively. Contamination with ammonium salts, nitrites, and phosphates is within 2.8-4.2, 1.5-2.3, and up to 1.9 MPC, respectively. The content of petroleum products is around 1.8 MPC.

Previously, we published the results of the LLC Vladikavkaz Food Processing Plant wastewater analysis, which was performed after aeration and in 3, 6, 13, 22, and 40 days to determine the water composition and the change in the concentrations of biomass, manganese, and iron [2].

In further studies, the task was set to analyze the wastewater composition after preliminary removal of heavy metals.

The study objective was to purify the agro-industrial complex wastewater from heavy metal compounds, which would improve the chemical composition of the Terek River basin and the Caspian Sea and, consequently, its flora and fauna.

2. Experimental research results

Heavy metals were previously removed from the original water (w_2) by alkalization. KOH was added to original wastewater w_1 to alkalize it. The precipitate obtained was filtered, and H_2SO_4 added to adjust pH=7.5–8.0. As a result, pH=8.0 was reached. Then, the composition of wastewater w_2 obtained has been determined, the results of which are given in Table 1.

| Indicator | Unit of Measure | Concentration before | Concentration after |
|-----------|-----------------|----------------------|---------------------|
| pH        | –               | 6.5                  | 8.0                 |
| BOD_5     | mg O_2/L        | 3.5                  | 3.5                 |
| COD       | mg O_2/L        | 1,526.7              | 1,526.7             |
| BOD_5: COD| %               | 0.2                  | 0.2                 |
| N-NH_4^-  | mg/L            | 6.0                  | 6.0                 |
| N-NO_2^-  | mg/L            | 0.003                | 0.003               |
| N-NO_3^-  | mg/L            | 1.3                  | 1.3                 |
| P-PO_4^{3-}| mg/L           | 0.41                 | 0.41                |
| Fe_3^+    | mg/L            | 2.9                  | 0.033               |
| Mn total  | mg/L            | 0.5                  | 0.29                |
| Suspended substances | mg/L | 30                  | 30                  |

After removing heavy metals, wastewater was aerated. Its composition was determined in 3, 6, 13, and 16 days. The wastewater w_2 chemical and biological composition study results are given in Tables 2, 3, 4, and 5. On the 21st day, the oxidizing capacity of the w_2 substrate was determined (Table 8).

Table 2. Wastewater w_2 Analysis Results after Preliminary Removal of Heavy Metals on the 3rd Day of Aeration.

| Indicator | Unit of Measure | Concentration |
|-----------|-----------------|---------------|
| pH        | –               | 7.5           |
| BOD_5     | mg O_2/L        | 0.5           |
| COD       | mg O_2/L        | 608           |
| BOD_5: COD| %               | 0.0008        |
N-NH$_4^+$ mg/L 15  
N-NO$_2^-$ mg/L 0.06  
N-NO$_3^-$ mg/L 0.18  
P-PO$_4^{3-}$ mg/L 1.018  
Fe$_{3+}$ mg/L 0.025  
Mn total mg/L 0  
Suspended substances mg/L 37

Table 3. Wastewater w$_2$ Analysis Results after Preliminary Removal of Heavy Metals on the 6th Day of Aeration.

| Indicator      | Unit of Measure | Concentration |
|----------------|-----------------|---------------|
| pH             | –               | 8.3           |
| BOD$_5$        | mg O$_2$/L      | 4             |
| COD            | mg O$_2$/L      | 128           |
| BOD$_5$: COD   | %               | 0.031         |
| N-NH$_4^+$     | mg/L            | 19            |
| N-NO$_2^-$     | mg/L            | 0.05          |
| N-NO$_3^-$     | mg/L            | 0.18          |
| P-PO$_4^{3-}$  | mg/L            | 1.36          |
| Fe$_{3+}$      | mg/L            | 0.103         |
| Mn total       | mg/L            | 0.67          |
| Suspended substances | mg/L | 250 |

Table 4. Wastewater w$_2$ Analysis Results on the 13th Day of Aeration.

| Indicator      | Unit of Measure | Concentration |
|----------------|-----------------|---------------|
| pH             | –               | 7.5           |
| BOD$_5$        | mg O$_2$/L      | 12            |
| COD            | mg O$_2$/L      | 64            |
| BOD$_5$: COD   | %               | 0.19          |
| N-NH$_4^+$     | mg/L            | 15.5          |
| N-NO$_2^-$     | mg/L            | 0.102         |
| N-NO$_3^-$     | mg/L            | 0.36          |
| P-PO$_4^{3-}$  | mg/L            | 2.21          |
| Fe$_{3+}$      | mg/L            | 0.09          |
| Mn total       | mg/L            | 0.45          |
| Suspended substances | mg/L | 250 |

Table 5. Wastewater w$_2$ Analysis Results on the 16th Day of Aeration.

| Indicator      | Unit of Measure | Concentration |
|----------------|-----------------|---------------|
| pH             | –               | 6.3           |
| BOD$_5$        | mg O$_2$/L      | 16.0          |
| COD            | mg O$_2$/L      | 508.9         |
| BOD$_5$: COD   | %               | 0.031         |
| N-NH$_4^+$     | mg/L            | 15.0          |
| N-NO$_2^-$     | mg/L            | 0.048         |
| N-NO$_3^-$     | mg/L            | 3.06          |
| P-PO$_4^{3-}$  | mg/L            | 0.7           |
| Fe$_{3+}$      | mg/L            | 0             |
| Mn total       | mg/L            | 0.149         |
| Suspended substances | mg/L | 280 |
The results of the study of the changes in the concentration of biomass, manganese, and iron in wastewater \( w_2 \) after preliminary removal of heavy metals for 16 days of aeration are given in Table 6.

**Table 6.** The Change in the Concentration of Biomass, Manganese, and Iron in Wastewater \( w_2 \) for 16 Days of Aeration.

| Days       | Unit of Measure | Concentration of Suspended substances | \( \text{Mn}_{\text{total}} \) | \( \text{Fe}^{3+} \) |
|------------|-----------------|--------------------------------------|-----------------------------|------------------|
| Initial data | mg/L            | 30                                   | 0.29                        | 0.033            |
| 3          | mg/L            | 35                                   | 0                           | 0.083            |
| 6          | mg/L            | 250                                  | 0.674                       | 0.103            |
| 13         | mg/L            | 250                                  | 0.45                        | 0.09             |
| 16         | mg/L            | 280                                  | 0.149                       | 0                |

The results of the study of the changes in the concentration of biomass in original wastewater \( w_1 \) and wastewater \( w_2 \) after preliminary removal of heavy metals during aeration are given in Table 7.

**Table 7.** The Change in the Concentration of Biomass in the Original Wastewater \( w_1 \) and Wastewater \( w_2 \) during Aeration.

| Days       | Unit of Measure | Concentration \( w_1 \) | Concentration \( w_2 \) |
|------------|-----------------|--------------------------|--------------------------|
| Initial data | mg/L            | 30                       | 30                       |
| 3          | mg/L            | 20                       | 35                       |
| 6          | mg/L            | 3                        | 250                      |
| 13         | mg/L            | 700                      | 250                      |
| 16         | mg/L            | 20                       | 280                      |
| 22         | mg/L            | 10                       | 320                      |
| 30         | mg/L            | 20                       | 450                      |

**Table 8.** Changes in the Original Wastewater \( w_1 \) Composition after Preliminary Removal of Heavy Metals during Oxidation under Contact Conditions.

| Item No. | Indicator | Unit of Measure | Initial Wastewater \( w_1 \) | After Daily Aeration |
|----------|-----------|-----------------|-----------------------------|----------------------|
| 1        | pH        | –               | 8                           | 7                    |
| 2        | \( \text{BOD}_5 \) | mg O\(_2\)/L | 3.5                         | 0.5                  |
| 3        | COD       | mg O\(_2\)/L    | 1,526.7                     | 608                  |
| 4        | \( \text{BOD}_5: \text{COD} \) | % | 0.2                         | 0.0008               |
| 5        | N-\( \text{NH}_4 \) | mg/L | 6.0                         | 15                   |
| 6        | N-\( \text{NO}_2 \) | mg/L | 0.003                       | 0.06                 |
| 7        | N-\( \text{NO}_3 \) | mg/L | 1.3                         | 0.18                 |
| 8        | P-\( \text{PO}_4 \) | mg/L | 0.41                        | 1.018                |
| 9        | \( \text{Fe}^{3+} \) | mg/L | 0.033                       | 0.025                |
| 10       | \( \text{Mn}_{\text{total}} \) | mg/L | 0.29                        | 0                    |
| 11       | Suspended substances | mg/L | 0.03                        | 0.037                |
The results of the study of the original wastewater composition after preliminary removal of heavy metals during oxidation under contact conditions are given in Table 8.

3. Conclusion
Based on the data obtained, the following conclusions have been made:

1. Preliminary removal of heavy metals reduces the inhibition of biochemical reactions. This allows continuously growing biomass.

2. Heavy metals do not affect different strains of microorganisms similarly. Young cells of microorganisms in the age of up to 13 days react less to heavy metals than active sludge in the age of 20-22 days.

3. Active sludge in the age of 13-22 days reacts more strongly to heavy metals in water, the lysis of certain strains of microorganisms is observed, which leads to an increase in biogenic elements in the water being treated.

4. References
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