Monitoring the state of water from water source and wastewater by the content of manganese (II) and iron (III) ions

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Abstract. The state of the water of water source and wastewater was monitored by indicators of mass concentrations of manganese (II) and iron (III) ions. Studies are based on data from decade (10 days) analyses. Combination of correlation and regression analysis and a time-series analysis method revealed factors leading to appearance and accumulation of manganese (II) and iron (III) ions in wastewater. A mathematical dependence is proposed for predicting the content of manganese (II) and iron (III) ions in the wastewater of soda ash production. By the method of time series analysis, it was found that the content of manganese ions (II) in wastewater does not depend on seasonality, but the content of iron ions (III) has a seasonal nature. The data obtained indicate the need for additional wastewater treatment systematically from manganese (II) ions and seasonally from iron (III) ions.

The vast majority of enterprises including the production of soda ash have come across the problem of limited natural resources, in particular, limestone raw materials. The surface reserves of raw materials are exhausted; deep reserves have to be developed where the raw materials are already of bottom quality. The increasing need for soda ash leads to an increase in the load on treatment plants.

Designing and erection of new treatment facilities is expensive and time consuming. Therefore, the identification of possible sources of environmental pollution by various compounds and the development of solutions to minimize their impact on the environment without complex additional techniques are practical and important [1,2].

The state of the water from water source and wastewater was monitored by indicators of mass concentrations of manganese (II) and iron (III) ions. The determination of mass concentration of total iron in natural and waste waters as well as of manganese was carried out according to the methods [3,4].

The studies are based on data from decade (10 days) analyzes over 3 years. The initial data are averaged; each month is divided into three periods, characterized by the value of indicator, calculated as the arithmetic average of 3 measurements. Each value obtained in this way is assigned a serial number starting with one.

Thus, sequences are formed that represent time series and consist of 144 values. The resulting series have strict time limits - each 36 values per year, which determines their seasonality period. Seasonal decomposition of the content of iron and manganese ions was carried out according to the formula (1).

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X_i = d_i + \varepsilon_i = (t_{i1} + s_i) + \varepsilon_i,
\]

(1)
where $X_t$ - elements of the time series; $d_t$ - deterministic component; $\varepsilon_t$ - random component; $t_r + c_t$ - trend-cyclic component; $s_t$ - seasonal component; $t = 1, ..., n$ - serial numbers of elements of the time series.

Studies of the influence of various types of trends on the values of seasonal indices in the seasonal decomposition procedure show that the use of a moving average, of stepwise function of average annual values and long-term annual average values as a trend does not affect the calculated values of seasonal indices, while the trend values differ slightly. This allows us to consider the long-term annual average values of indicators as a trend and proceed to the consideration of deterministic component within the annual cycle.

Thus, the convolution of the time period (4 years) to the “hypothetical” year which is a model of the time period was carried out. The deterministic components describe the regular changes in the mass concentration of manganese (II) and iron (III) ions in the river water and wastewater in the annual cycle (figures 1, 2, 3); wherein the values with numbers ($i = 1-3$) correspond to January, ($i = 4-6$) to February, etc.

**Figure 1.** Deterministic components of time series of manganese in the river Belaya.

**Figure 2.** Deterministic components of time series of manganese after the pilot plant.
The analysis of the changes in the deterministic component of manganese in water of water source shows that in the period (i = 10–12; 14–15; 33–34) it rises to 0.115 and does not have any dependence and seasonal character.

The results of contribution of the trend, seasonality and the random component to the total variability of indicators of manganese ions (II) compounds are shown in Table 1.

**Table 1. Contribution of components to the variability of the content of manganese ions (II) in the water source and wastewater.**

| Manganese ions (II)     | Contribution of component, % |
|-------------------------|------------------------------|
|                         | Trend | Seasonal | Random  |
| In the river water      | 16,7  | 18,5     | 64,5    |
| In the wastewater       | 13,1  | 20,0     | 66,9    |

**Figure 3.** Deterministic component of time series of iron after the pilot plant.

**Table 2.** Contributions of components to the variability of the index of iron ions (III) in the river water and wastewater.

| Iron ions (III)     | Contribution of component, % |
|---------------------|------------------------------|
|                     | Trend | Seasonal | Random  |
| In the river water  | 5,8   | 64,9     | 29,4    |
| In the wastewater   | 4,6   | 62,0     | 33,5    |

From the annual period, the “unstable period” (i = 9–16) can be distinguished from the values of the deterministic components, in which iron ions (III) in river water and water flow increase, i.e. in the flood period. Starting from i = 17, mass concentration of iron ions (III) is practically more stable.

The analysis of change in the deterministic component of manganese ions (II) in river water over the year shows that in the period (i = 7–13; 14 = 16; 33–35), its concentration rises to 0.11 mg/dm³; the largest increase in wastewater up to 0.16 mg/dm³ is observed in the period (i = 13–17).
While the changes in the mass concentration of iron ions (III) are seasonal and the highest content in river water and water flow is observed approximately at the same time, then the change in the mass concentration of manganese ions (II) in the water has no seasonality, and the maximum content in river water and wastewater appears at different periods.

Thus, the change in the mass concentration of iron ions (III) in wastewater is seasonal in nature, as in the river water. This circumstance allows us to consider that the pollution of water flows by ions of a given metal depends on the quality of river water. The change in manganese ions (II) in wastewater is not seasonal and does not depend on the concentration of manganese ions (II) in river water. The data obtained indicate the need for additional wastewater treatment systematically from manganese ions (II) and seasonally from iron ions (III) [5-8].

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