Heavy metals absorption by excessive activated sludge of biological treatment facilities

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Abstract. The study was conducted at the biological treatment facilities of Veliky Novgorod. It has been established that the main percentage of metals is contained in the organic component of the conditionally solid phase of excess activated sludge. Based on the study of the elemental composition of the excess activated sludge, it is concluded that organic compounds containing aromatic, aliphatic and amine-containing functional groups are very diverse in the excess activated sludge. Main classes of substances making up the excess activated sludge are established. The mass fractions of the main classes of organic compounds established by the rational method are in good agreement with the analysis of the main classes of organic compounds that make up the excess activated sludge of biological treatment plants. The main compounds making up the inorganic component of the conditionally solid phase of excess activated sludge are determined. The study reveals a large variety of both organic and inorganic compounds in the excess activated sludge, which are able to bind heavy metal ions from aqueous medium due to physical and chemical interactions.

1. Introduction
The development of a rational technology for the disposal of excess activated sludge from biological treatment facilities requires studying the heavy metals absorption patterns and forms of their binding with the main components of excess activated sludge. Known data characterizing the process of heavy metals extraction by excess activated sludge from aqueous medium and their accumulation in it are contradictory and not systematized, which requires a study of absorption processes with the aim of further developing a method for heavy metals extraction from excess activated sludge at biological treatment plants [1–6].

2. Materials and methods
The study on the heavy metals absorption by excess activated sludge during biological wastewater treatment was carried out at biological treatment plants in Veliky Novgorod. The concentration of metals was determined by atomic absorption spectroscopy [7]. The main classes making up the excess activated sludge were investigated by a rational analysis method [8]. The main classes of organic compounds were determined by mass spectrometric method [9]. The composition of inorganic compounds - on an x-ray diffractometer [10].
3. Results and discussion

In order to study the basic laws of heavy metals absorption processes in the excess activated sludge, the gross concentrations of metals in the excess activated sludge at biological treatment plants are analyzed (table 1).

**Table 1.** Gross concentrations of metals in excess activated sludge of biological treatment facilities (mg/kg of absolutely dry matter).

| Metal | Zn   | Mn   | Cr | Fe       | Cu  |
|-------|------|------|----|----------|-----|
| Excess activated sludge | 2350 | 1100 | 115| 23700    | 975 |

The example of copper and manganese shows the distribution of metals in the liquid and conditionally solid phases of the excess activated sludge in organic and inorganic components (table 2).

**Table 2.** Proportion of metals (copper and manganese) in the initial excess active sludge of biological treatment facilities.

| Metal | Proportion of metals in the liquid and solid phases of excess activated sludge, % of the gross concentration of metals |
|-------|-------------------------------------------------------------------------------------------------|
|       | Liquid phase                                      | Conditionally solid phase                                      |
|       | Organic component | Inorganic component | Organic component | Inorganic component |
| Cu    | 5.0          | 6.0               | 73.0               | 16.0               |
| Mn    | 3.0          | 10.0              | 78.0               | 9.0                |

The table shows that in the initial excess activated sludge, the main percentage of both copper and manganese are in the organic component of the conditionally solid phase of excess activated sludge.

The excess activated sludge composition at the biological treatment facilities is not constant and varies depending on the culture growth stage and the composition of the utilized substrate, as evidenced by the specific chemical oxygen consumption. In our studies, it ranged from 1.27–1.42 mg O₂/kg of absolutely dry ash-less matter (average value – 1.34 mg O₂/kg of absolutely dry ash-less matter), which is in good agreement with the excess activated sludge rounded formula C₅H₇O₂N.

The metals concentration in the excess activated sludge at biological treatment facilities per unit of specific chemical oxygen consumption is presented in table 3.

**Table 3.** Metals concentration in the excess activated sludge per unit of specific chemical oxygen consumption.

| Excess activated sludge | Zn | Mn | Cr | Fe | Cu |
|-------------------------|----|----|----|----|----|
|                         | 1754| 821| 86 | 17687 | 728 |

The elemental composition of excess activated sludge of biological treatment facilities is presented in table 4.
Table 4. Mass fraction of the main elements in the excess activated sludge of biological treatment facilities in terms of ash-less substance.

| Object                  | Mass fraction of main elements in excess activated sludge, % | Atomic ratios |
|-------------------------|-------------------------------------------------------------|---------------|
|                         | C    | H    | N    | O    | O/C  | H/C  | N/C  |
| Excess activated sludge | 47.0 | 8.0  | 7.0  | 38.0 | 0.81 | 0.17 | 0.15 |

High mass fractions of carbon and nitrogen in the excess activated sludge, as well as their atomic ratios suggest a large variety of organic compounds containing aromatic, aliphatic and amine-containing functional groups in the excess activated sludge.

To study the main classes of substances making up the excess activated sludge, a rational analysis is carried out, the essence of which is shown in figure 1.

![Sludge organic matter fractionation scheme](image)

**Figure 1.** Sludge organic matter fractionation scheme.
The results of studying the chemical composition of excess activated sludge by the rational method are presented in Table 5.

**Table 5.** Mass fraction of the main classes of compounds in excess activated sludge of biological treatment facilities.

| Main classes of compounds in excess activated sludge | Mass fraction, % |
|-----------------------------------------------------|------------------|
| Fats and fat-like substances                         | 17.0             |
| Carbohydrates                                       | 26.0             |
| Proteins and protein-like substances                 | 28.0             |
| Humic acids                                         | 1.0              |
| Inorganic compounds                                 | 28.0             |

The analysis of the main classes of organic compounds constituting the excess activated sludge at biological treatment plants carried out by mass spectrometric analysis is shown in Table 6.

**Table 6.** Mass fraction of main classes of organic compounds constituting excess activated sludge at biological treatment plants, in terms of ash-less substance.

| Main classes of organic compounds constituting excess activated sludge | Mass fraction in terms of ash-less substance, % |
|-----------------------------------------------------------------------|-----------------------------------------------|
| Aliphatic carboxylic and hydroxycarboxylic acids                      | 3.0                                           |
| Phenols                                                               | 0.5                                           |
| Aldehydes, ketones                                                    | 0.4                                           |
| Alcohols                                                              | 0.6                                           |
| Fulvic acids                                                          | 0.7                                           |
| Humic acids                                                           | 0.4                                           |
| Polyphenols                                                           | 0.3                                           |
| Reducing sugars                                                       | 2.4                                           |
| Polysacharoses                                                        | 32.0                                          |
| Amino acids                                                           | 1.1                                           |
| Protein-like substances                                               | 36.6                                          |
| Compound ethers                                                       | 22.0                                          |

The inorganic component of excess activated sludge is about 30%. The inorganic component of the excess activated sludge of biological treatment plants was examined on an X-ray diffractometer X’Pert Pro of Philips (figure 2).

The analysis of the X-ray diffraction pattern of the inorganic component of the conditionally solid phase of the excess activated sludge made it possible to establish the basic compounds making up the inorganic component of its conditionally solid phase:

- quartz sand – SiO₂;
- magnetite – Fe₃O₄;
- muscovite – (K, Na)Al₂(Si, Al)₄O₁₀(OH)₂;
- illite – KAl₂(Si₂Al)O₁₀(OH)₂;
- calcium and magnesium phosphates – Ca₉Fe(PO₄)₇, Ca₁₈Mg₂H₂(PO₄)₁₄, Ca₉FeH₀.₅(PO₄)₇.
Thus, the study reveals a large variety of both organic and inorganic compounds in excess activated sludge, which are able to bind heavy metal ions from aqueous media due to their physical and chemical interaction.

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