The sustainable utilization of malting industry wastewater biological treatment sludge

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Abstract. The article deals with the research of using the sludge from malting industry wastewater’s biological treatment and the calcium carbonate slurry as organo-mineral fertilizing additives. The sludge, generated as a result of industrial wastewater biological treatment, is subject to dumping at solid domestic waste landfills, which has a negative impact on the environment, though its properties and composition allow using it as an organic fertilizer. The physical and chemical properties of both wastes have been studied; the recommendations concerning the optimum composition of soil mix, containing the above-mentioned components, have been provided. The phytotoxic effect on the germination capacity and sprouts of cress (Lepidium sativum), barley (Hordeum vulgare) and oats (Avena sativa) in soil mixes has been determined. The heavy metals and arsenic contents in the sludge does not exceed the allowable level; it is also free of pathogenic flora and helminthes.

1. Introduction
The amount of wastewater sludge is constantly growing, as a result of, firstly, the population growth and, secondly, the increase of demand for water resources. The increase of wastewater sludge amount causes environmental problems, as well as the problems of its economically efficient and environmentally sound utilization. There are a number of regions in the Russian Federation where there exists a threat of environmental, sanitary and epidemiological degradation and occurrence of emergency situations due to possible accidents at waste treatment facilities, aeration plants or containment ponds [1].

At present 20·109 tons of wastewater sludge per year is generated in the world [2]. In Russia, the generation of wastewater sludge amounts to 100 million tons per year, with moisture level 98%, i.e. 2 million tons per year in dry matter [3]. In Europe, the amount of wastewater sludge generation is decreasing, despite the high development rates [4]. Of various types of waste disposal, the most common way of wastewater sludge utilization in Russia is its burial or permanent disposal at sludge draining beds. The usage of sludge as a fertilizer is no more than 4–6 % of its total amount [5]. As using sludge as a fertilizer can contaminate soils and plants with various forms of heavy metals, the sludge must be treated and purified from heavy metals before usage [6]. According to the resulting data, the recommended amount of adding the mixed mechanical and biological treatment sludge to the soil for wheat and barley is 30–40% [7]. It was found that, long-term application of sewage sludge may lead to accumulation of Zn, Cu and Ni in soil and plants [8]. A possible method of disposal is the use of sludge or ash in cement and concrete, obtaining from it the use of biogas or as fuel due to the content of organic matter after drying [9–11].
2. Material and methods
The object of research waste is referred to as «The excess dewatered sludge of malting industry wastewater». According to the results of quantitative chemical analysis, this waste contains the following components (table 1). The annual generation of the waste amounts to about 2200 tons per year. It is generated as a result of industrial wastewater biological treatment at one of the Belgorod region malting enterprises (waste water after washing and steeping of barley, removing of float and spraying barley in tanks, cleanup of steeping tanks and malting equipment) and the subsequent dewatering of the excess activated sludge with a flocculation agent on a filter-belt press. At present, it is subject to landfilling.

Table 1. The composition of malting industry wastewater biological treatment sludge.

| Component           | Content, % |
|---------------------|------------|
| Moisture            | 81.20      |
| Organic matter      | 16.98      |
| Iron oxide          | 0.390      |
| Aluminium oxide     | 0.003      |
| Sulphates           | 0.417      |
| Nitrates            | 0.003      |
| Calcium oxide       | 0.690      |
| Magnesium oxide     | 0.021      |
| Phosphates          | 0.150      |
| Chlorides           | 0.005      |
| Nickel              | 0.005      |
| Cadmium             | 0.0001     |
| Lead                | 0.001      |
| Ash                 | 0.1349     |

The heavy metals and arsenic content in the sludge does not exceed the allowable level (table 2). According to GOST R 17.4.3.07-2001 [12] the biological treatment sludge belongs to the first class, which means that it can be used for all species of agricultural crops (except for vegetables, mushrooms, greenstuff and strawberry). It is also suitable for technical and biological recultivation of contaminated soils, by its heavy metals content according to GOST R 54534-2011 [13]. Its microbiological and parasitological indices are within the allowable limits (table 3); as a result of the analysis, there were detected no pathogenic flora or helminthes in the sludge. By the negative impact on the environment, the sludge refers to category IV (low-hazardous substance) [14], which has been determined with two test objects (table 4).

Table 2. Heavy metals content in the biological treatment sludge.

| Component | Dry matter concentration, mg kg⁻¹, not above Sediment group I [12] | Sediment group II [12] | Sediment under research, mg kg⁻¹ of dry matter |
|-----------|------------------------------------------------------------------|-------------------------|-----------------------------------------------|
| Lead      | 250                                                              | 500                     | 3.59                                          |
| Cadmium   | 15                                                               | 30                      | 0.261                                         |
| Nickel    | 200                                                              | 400                     | 19.34                                         |
| Chrome    | 500                                                              | 1000                    | 12.59                                         |
| Zinc      | 1750                                                             | 3500                    | 601.40                                        |
| Copper    | 750                                                              | 1500                    | 51.95                                         |
| Mercury   | 7.5                                                              | 15                      | 0.080                                         |
| Arsenic   | 10                                                               | 20                      | 1.46                                          |
Another waste product studied in this work was the waste of chalk production – the calcium carbonate slurry, which has no toxicity properties (as determined with two test objects); its generation amounts to 17000 tons per year. The slurry moisture was 60–70%.

**Table 3.** Microbiological and parasitological indices.

| Index                                | Measure unit | Content          | Guideline value |
|--------------------------------------|--------------|------------------|-----------------|
| General coliform bacteria            | Cells g⁻¹    | Less than 10     | 100             |
| Pathogenic enterobacteria            | Cells g⁻¹    | Not detected     | Not allowed     |
| Viable helminthes eggs and larvae    | Specimen kg⁻¹| Not detected     | Not allowed     |
| Enteric pathogenic protozoa cysts    | Specimen g⁻¹ | Not detected     | Not allowed     |

**Table 4.** The toxicological analysis data of a sample of waste referred to as «The excess dewatered sludge of malting industry wastewater».

| Method                          | Test object       | Test length, hours | Target parameter | Dilution factor, times |
|---------------------------------|-------------------|--------------------|-------------------|------------------------|
| Mortality and fertility test    | *Ceriodaphnia affinis* | 48                 | presence          | LDF₆₀⁻⁴₈⁻¹               |
|                                 |                   |                    | absence           | SDF₆₀⁻⁴₈⁻¹₀₀           |
| The testing culture optical     | *Chlorella vulgaris Beijer* | 22                 | presence          | IDF₅₀⁻²₂⁻¹              |
| density measurement             |                   |                    | absence           | SDF₂₀⁻²₂⁻¹₀₀           |

*LDF – lethal dilution factor, SDF – safe dilution factor, IDF – inhibiting dilution factor*

The composition of chalk production waste – the calcium carbonate slurry without regard to moisture is presented in table 5. The waste is diluted with process water and channeled to the industrial sewage, then to the tailing flume of the concentration plant and then by chute to the tailing dump. The water is separated from the slurry by natural filtration and flows to the lower level of the tailing dump, and then is used again in production. The slurry is not used.

**Table 5.** The slurry composition without regard to moisture

| Component     | Content, % |
|---------------|------------|
| Nickel        | 0.0060     |
| Iron trioxide | 0.0420     |
| Calcium carbonate | 64.500    |
| Chrome        | 0.0001     |
| Manganese     | 0.0210     |
| Silicium dioxide | 35.4196  |
| Cadmium       | 0.0002     |
| Copper        | 0.0016     |
| Zinc          | 0.0075     |
| Lead          | 0.0020     |

The soil was collected at the territory of BSTU named after V G Shukhov in October 2015. The heavy metals and arsenic content was analyzed according to the methodologies of their detection in agricultural field soils and crop products and by the photometric method of detecting arsenic in soils;
the results are presented in table 6. The pH of salt extract (for potassium chloride) amounted to 6.8 (at the standard rate $\text{pH}_{\text{KCl}} > 5.5$). The content of components in the soil: humus – 4.9%; hydrolyzable nitrogen – 151 mg/kg; labile phosphorus – 43 mg kg$^{-1}$; mobile potassium – 530 mg kg$^{-1}$.

Table 6. Analysis data of heavy metals and arsenic content in the soil

| Component | Pb | Cd | Ni | Cr | Zn | Hg | As |
|-----------|----|----|----|----|----|----|----|
| TPC$^a$ for soil, $\text{pH}_{\text{KCl}} > 5.5$ | 130 | 2.0 | 80 | No | 220 | 2.1 | 10 |
| The soil under research | 15.40 | 0.332 | 22.81 | 21.29 | 32.43 | 0.025 | 3.23 |

$^a$ Tentative permissible concentration

3. Results and discussion

The components (slurry, soil and sludge) were mixed at various ratios; the calcium carbonate slurry concentration amounted to 1 %. The biological treatment sludge and the calcium carbonate slurry were dried before use. The biological treatment sludge content amounted to, % of mixture weight: 10.0; 20.0; 30.0; 40.0; 50.0 and 100 %; the pH value of aqueous extract amounted to: 7.56; 7.30; 7.15; 7.12; 7.08 and 7.58 respectively.

In the course of the experiment, 60 seeds of cress Lepidium sativum (Cruciferae family) were planted into vegetation vessels and the dependence of germination capacity and sprouts length on the content of biological treatment sludge in the soil mix was researched. All the experiments were carried out in triplicate. As a result of the research there was determined the germination capacity and sprouts length on the 4, 6, 8 and 12 day of the experiment (figure 1 and 2).

For growing cress, the sludge content in the soil mix must not exceed 20 %. As depicted from the presented data, the sprouts length becomes smaller with the increase of the sludge concentration. This indicates its phytotoxic effect. At the same time, it belongs to the first class according to GOST R 17.4.3.07-2001 [12]. The possible factor of the biological treatment sludge adverse effect is, that due to its being a waste, the established allowable level of metals content in the sludge was based on sanitation and hygiene standards, and don’t take into account the phytotoxic effect on the plants. The nitrate content in the sludge and soil mixes was determined by ionometric technique (table 7). The acceptable level of nitrate content in the soil according to hygienic standards is 130 mg kg$^{-1}$. The high nitrate concentration in the soil is absolutely safe and not toxic for plants – on the contrary, it fosters the growth of aerial parts of plants, makes the photosynthesis process more active, but in the given concentrations it is a constraining factor.
Table 7. Nitrate concentration in soil mixes and in the biological treatment sludge.

| The percentage of sludge in the mix, % | 0.0 (the initial soil) | 10.0 | 20.0 | 30.0 | 40.0 | 50.0 | 100.0 (sludge) |
|-------------------------------------|-------------|------|------|------|------|------|----------------|
| Nitrate, mg kg⁻¹                   | 30.9       | 372.0 | 662.0 | 1626.0 | 1742.0 | 2200.0 | 2468.0         |

At 10.0 and 20.0 % of biological treatment sludge in the soil mix the germination capacity of *Lepidium sativum* is increased by about 5.0 and 10.0 % respectively. At adding 30.0 % of sludge to the soil the germination capacity index decreases to that of the initial soil. In the soil mix with 30.0 % of sludge the germination capacity is reduced to the level of the initial soil; at 40.0 % of sludge the seeds germination capacity drops considerably, and at 50.0 % approaches zero.

The other crop plants used in the experiment were barley (*Hordéum vulgáre*) and oats (*Avena sativa*). 100 selected seeds of each species were planted to separate vegetation vessels. The experiment was carried out in triplicate. According to the results of germination index fixation, the recommended content of sludge in the soil for oats and barley amounts to 20.0–30.0 %. The germination indices of *Hordéum vulgáre* and *Avena sativa* seeds are presented in figure 3 and 4.

![Figure 3](image1.png) **Figure 3.** The dependence of *Hordéum vulgáre* seeds germination capacity on the biological treatment sludge content in soil mixes.

![Figure 4](image2.png) **Figure 4.** The dependence of *Avena sativa* seeds germination capacity on the biological treatment sludge content in soil mixes.

In figure 5 and 6, the dependence of *Hordéum vulgáre* and *Avena sativa* sprouts length on the biological treatment sludge content in soil mixes is presented.

![Figure 5](image3.png) **Figure 5.** The dependence of *Hordéum vulgáre* sprouts length on the biological treatment sludge content in soil mixes

![Figure 6](image4.png) **Figure 6.** The dependence of *Avena sativa* sprouts length on the biological treatment sludge content in soil mixes

With the increase of sludge content (10.0 and 20.0 %) in the soil mix, the sprouts length increases as well, and then the growth slows down. At the sludge content 40.0 and 50.0 % the growth is inhibit-
ed. In the vegetation vessel with 100.0% of sludge the sprouts length of both species amounted to about 5–6 cm on the 18th day (at 20.0 % of sludge the sprouts length on the 18th day was 27 cm at average). So, the largest herbage length was observed in those plants, which were grown in the soil mix with 20.0 % of sludge.

The phytotoxic effect of biological treatment sludge on grain crops, according to its content in the soil by weight for a vegetation vessel was calculated. As we can see in the presented diagrams (figure 7 and 8), the stimulating effect on barley is observed at the sludge content in the soil mix up to 30%, and on oats – at the sludge content up to 40%.

**Figure 7.** The stimulating and phytotoxic effect of soil mixes with biological treatment sludge and calcium carbonate slurry on the sprouts of *Hordëum vulgåre* (by weight for a vegetation vessel)

**Figure 8.** The stimulating and phytotoxic effect of soil mixes with biological treatment sludge and calcium carbonate slurry on *Avena sativa* (by weight for a vegetation vessel)

*Hordëum vulgåre* is more sensitive to the content of biological treatment sludge. At the sludge content over 40% the phytotoxic effect is observed, which can be calculated by the following formula:

\[
PE = \frac{m_c - m_x}{m_c} \times 100%
\]

where \(m_c\) – the total weight of plants in the check vegetation vessel; \(m_x\) – the total weight of plants grown on the presumably phytotoxic medium.

### 4. Conclusion

As it has been mentioned above, the organo-mineral fertilizer is presented in the form of mixture. Before use, the biological treatment sludge is mixed with the calcium carbonate slurry, and the obtained mixture is pelletized. The initial components are fed from hoppers to the belt conveyor, then through a funnel to the paddle double-shaft mixer, and then to the pelleting mill. Then the pelletized mixture is dried, and after that, the finished product can be sent to storage facilities or to the customers.

The process scheme (figure 9) consists of five process units and appears as consecutive schematic drawings of interconnected machines and equipment, presented on the scheme in form of simplified outlines of the elements, conventional signs, rectangles and other geometrical figures. The biological treatment sludge is generated unevenly throughout the year, so the presented scheme operates periodically. As the biological treatment sludge is accumulated, it can be prone to natural drying, which results in its shrinkage. The line performance is assumed as 8 tons per day. It is recommended to use the double spiral mixer, which provides the continuous organo-mineral fertilizer production process.
Figure 9. The process scheme of the organo-mineral fertilizer production: 1 – components storage unit; 2 – components transportation unit; 3 – mixing unit; 4 – pelletizing, drying and finished product unit.

The carried-out research has demonstrated the prospects of using the malting industry wastewater biological treatment sludge in amount of 20% of the soil mix, which corresponds to 20 t/ha. The process scheme of the organo-mineral fertilizer production has been designed. The saving of annual environmental charges because of prevention of sludge dumping will amount to 2 million 800 thousand rubles at 2016 values.

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