Phytoremediation as a method for cleaning sludge beds of biological treatment plants from heavy metals

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Abstract. The aim of this study is to select a phytoremediation plant for cleaning sludge beds of biological treatment plants from heavy metals. The study was conducted on sludge beds of biological treatment facilities of Veliky Novgorod with a sludge retention time of 1 year and 15 years. It is established that the forms of metals in the sludges and wastewater sludge depend on the nature of the metal. Manganese (II) predominantly binds to compounds that make up sludge and wastewater sludge by the ion exchange mechanism, copper (II) – by the complex formation mechanism, zinc (II) – is codeposited with calcium and magnesium carbonates, manganese (IV) and iron hydroxides (III). Six selected plants were analyzed (bedstraw, cow vetch, field daisy, silverweed cinquefoil, base vervain, winter cress), those growing on sludge beds with a sludge retention time of 15 years, for the content of copper (II), zinc (II) and manganese (II) in different parts of plants. The phytoremediation plant was selected according to the indicators of the coefficient of biological accumulation (coefficient of biological accumulation) and translocation factor. It has been established that the bedstraw can be called a universal phytoremediation plant, in the absence of significant sludge contamination with copper (II), it is most preferable to use base vervain. Selected phytoremediation plants can be used for artificial planting on sludge beds in order to further use these beds as fertile lands.

1. Introduction

Currently, disposal at landfills remains the main method for neutralization of sludges and wastewater sludge of biological treatment facilities (table 1) [1, 2]. Landfills (sludge beds) are environmentally hazardous objects due to pollution of soils, surface and ground waters, and of the atmosphere.

Many countries of the world are striving to reduce the proportion of wastewater sludge disposed of at landfills (sludge beds), but to increase the proportion of thermal and other methods of neutralization and disposal of sludge. The widespread use of thermal methods for disposal of wastewater sludge is due to the high content of heavy metals in them, as well as in the absence of approaches to the neutralization of heavy metals from quasi-solid technogenic formations.

| Table 1. Application of methods for neutralization and disposal of wastewater sludge from biological treatment plants in different countries. |
|----------------------------------|---------------------------------|-----------------|-----------------|------------------|
| Country                          | The share of the use of methods, % of the mass of sludge | Disposal at landfills (sludge beds) | Thermal methods | Biological methods | Other methods |
|----------------------------------|---------------------------------|-----------------|-----------------|------------------|-----------------|

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Russia & 97.0 & 1.7 & 1.0 & 0.3 \\
Austria & 69.5 & 9.0 & 18.5 & 3.0 \\
Great Britain & 89.0 & 9.5 & 1.4 & 0.1 \\
Belgium & 60.0 & 28.0 & 9.5 & 2.5 \\
Denmark & 27.5 & 70.0 & 0.5 & 2.0 \\
Italy & 58.5 & 24.0 & 10.5 & 7.0 \\
Canada & 80.0 & 19.0 & 1.0 & 0.0 \\
Poland & 95.0 & 1.0 & 2.5 & 1.5 \\
USA & 85.0 & 14.0 & 0.1 & 0.9 \\
France & 45.4 & 40.0 & 12.5 & 2.1 \\
Switzerland & 14.0 & 70.0 & 10.0 & 6.0 \\
Sweden & 43.5 & 44.0 & 10.5 & 2.0 \\
Japan & 27.0 & 70.0 & 0.3 & 2.7 \\

With the use of thermal method of disposal of wastewater sludge, atmospheric pollution occurs, which requires additional costs for a system for cleaning gas emissions from pollutants. The resulting ash contains high concentrations of heavy metals, which also requires well-thought-out systems for its disposal. With the use of the thermal method of sludge disposal, destruction of organic substances that make up their composition, which could be used to replenish soil humus, occurs [3, 4].

2. Materials and methods

The study was conducted on sludge beds of biological treatment facilities of Veliky Novgorod with a sludge retention time of 1 year and 15 years.

Excessive active sludges and sludge from biological treatment facilities are a complex multicomponent hydrophilic heterophase system. Heavy metals interact with compounds that are part of the excess active sludges and sludge formed in biological treatment plants, according to various mechanisms, among which the main ones can be distinguished [5, 6]:

1) adsorption: physical, chemical, ion exchange;
2) chemical interaction with organic and inorganic ligands by the complexation mechanism;
3) destructive and oxidative energy-chemical processes;
4) biological processes;
5) codeposition with Fe(OH)₃, MnO₂, CaCO₃ and MgCO₃.

The forms of presence of heavy metals in the sludges and wastewater sludge of biological treatment plants, due to the mechanisms mentioned above vary depending on the nature of the metals.

To find forms of binding of heavy metals with compounds that make up the sludges and wastewater sludge, the method of rational analysis was used. The metal concentration was determined by atomic absorption spectroscopy in the extract after each sequential extraction according to the scheme proposed by W. Miller (table 2) [7].

| Form of metal                                      | Extraitant                        |
|--------------------------------------------------|-----------------------------------|
| Water-soluble form                                | H₂O                               |
| Ion-exchange form                                 | 0.1 H.Ca(NO₃)₂                     |
| Chemical interaction according to the complexation | 0.1 M NaOH                         |
| mechanism                                        | 0.1 M NaOH, pH = 7                 |
| Codeposited with CaCO₃ and MgCO₃                  | 0.1 M NH₃OH·HCl in 0.01 M HNO₃    |
| Codeposited with MnO₂                              | 0.3 M sodium citrate in 1 M NaHCO₃|

Table 2. The scheme of rational analysis of sludges and wastewater sludge proposed by W. Miller.
### Table 3. Share (in % of gross content) of various forms of heavy metals in sludge.

| Form of metal                                      | Mass fraction of metals (in % of the total content) |
|---------------------------------------------------|-----------------------------------------------------|
|                                                   | Cu        | Mn       | Zn       |
| Water-soluble form                                | 3.2       | 7.1      | 3.5      |
| Ion-exchange form                                 | 15.2      | 57.1     | 20.8     |
| Chemical interaction according to the complexation mechanism | 39.7      | 18.1     | 14.1     |
| Codeposited with CaCO$_3$ and MgCO$_3$            | 16.6      | 4.8      | 28.5     |
| Codeposited with MnO$_2$                          | 10.8      | 2.8      | 20.8     |
| Codeposited with Fe(OH)$_3$                       | 3.4       | 3.6      | 3.8      |
| Non-dissolved residue                             | 11.1      | 6.5      | 8.5      |

3. Results and discussion

The results show (table 3) that the forms of metals in the sludges and wastewater sludge depend on the nature of the metals. So, for example, manganese (II) predominantly binds to compounds that make up the sludges and wastewater sludge by the ion exchange mechanism. The mass fraction of the ion-exchange form of manganese (II) is about 57%. Copper (II) is predominantly bound to the above mentioned compounds by the complexation mechanism. The mass fraction of copper (II) bound by the complexation mechanism is about 40%. Zinc (II) is more characteristic of codeposition with calcium and magnesium carbonates, manganese (IV) and iron (III) hydroxides. The mass fraction of zinc (II), codeposited with these components is about 50%.

Phytoremediation can be one of the effective methods for cleansing sludge beds from heavy metals. Using this method, it is possible to achieve maximum permissible values for the content of heavy metals in the soil, allowing for the use of sludge beds as fertile lands, given the low cost of work and the practical absence of negative environmental impacts.

Two directions for the use of phytoremediation plants can be proposed:

1. at high concentrations of heavy metals – plants can be burned, and the ash can be used to separate metals in pure form;
2. at low concentrations of heavy metals - use biomass of phytoremediation plants as fertilizers containing trace elements which are biologically important for plants [8, 9].

On the sludge beds of biological treatment plants, there are various types of plants. Sludge beds with retention time of 15 years are of great scientific interest. The concentrations of copper (II), manganese (II), and zinc (II) were determined in sludge beds and plants. In order to select phytoremediation plants, concentrations of heavy metals in sludge of sludge beds with retention time of 15 years, as well as in plants growing on these sludge beds, were determined. For comparison, data on the concentration of heavy metals in the sludge of sludge beds with retention time of 1 year are presented (table 4).

### Table 4. Gross metal content in sludge of sludge beds.

| Object                                  | Cu, mg/kg a.d.m. | Zn, mg/kg a.d.m. | Mn, mg/kg a.d.m. |
|-----------------------------------------|------------------|------------------|------------------|
| Sludge of 1 year of retention           | 740              | 1860             | 1214             |
| Sludge of 15 years of retention         | 55               | 220              | 110              |

Concentrations of heavy metals in various parts of plants (roots, leafage, culms, fruits) differ, and differ significantly (500-800 times) exceed the concentrations in the same parts of plants growing on soils not contaminated with heavy metals (tables 5, 6, 7).
Table 5. Concentrations of Cu_{total} (mg/kg of absolute dry matter) in the roots, culms, leafage and fruits of plants growing on sludge beds with a sludge with a retention time of 15 years.

| Plant species         | Root  | Culm | Leafage | Fruits |
|-----------------------|-------|------|---------|--------|
| Bedstraw              | 120   | 20   | 130     | 145    |
| Cow vetch             | 750   | 160  | 160     | –      |
| Field daisy           | 65    | 20   | 15      | 50     |
| Silverweed cinquefoil | 80    | 120  | 120     | –      |
| Base vervain          | 1240  | 70   | 70      | –      |
| Winter cress          | 150   | 100  | 100     | –      |

Table 6. Concentrations of Zn_{total} (mg/kg of absolute dry matter) in various parts of the plants of sludge beds with a sludge with a retention time of 15 years.

| Plant species         | Root  | Culm | Leafage | Fruits |
|-----------------------|-------|------|---------|--------|
| Bedstraw              | 2420  | 420  | 2681    | 3052   |
| Cow vetch             | 2175  | 110  | 110     | –      |
| Field daisy           | 1070  | 40   | 1240    | 35     |
| Silverweed cinquefoil | 70    | 110  | 110     | –      |
| Base vervain          | 1320  | 7230 | 7230    | –      |
| Winter cress          | 295   | 40   | 40      | –      |

Table 7. Concentrations of Mn_{total} (mg/kg of absolutely dry residue) in various parts of the plants of sludge beds with a sludge with a retention time of 15 years.

| Plant species         | Root  | Culm | Leafage | Fruits |
|-----------------------|-------|------|---------|--------|
| Bedstraw              | 195   | 80   | 160     | –      |
| Cow vetch             | 1000  | 375  | 375     | –      |
| Field daisy           | 550   | 22   | 610     | 21     |
| Silverweed cinquefoil | 675   | 200  | 200     | –      |
| Base vervain          | 80    | 600  | 600     | –      |
| Winter cress          | 50    | 155  | 155     | –      |

To identify phytoremediation plants, the coefficient of biological accumulation and translocation factor were calculated.

The coefficient of biological accumulation (CBN) was calculated by the formula:

\[
\text{CBN} = \frac{C_{\text{plant}}}{C_{\text{soil}}} \quad (1)
\]

where: \( C_{\text{plant}} \) is the concentration of heavy metal accumulated by the plant, mg/kg of absolute dry matter; \( C_{\text{soil}} \) is the concentration of heavy metal determined in the soil, mg/kg of absolute dry matter.

Translocation factor (TF), calculated by the formula:

\[
\text{TF} = \frac{C_{\text{terr.}}}{C_{\text{root}}} \quad (2)
\]

where: \( C_{\text{terr.}} \) is the concentration of heavy metal in the terrestrial part of the plant, mg/kg of absolute dry matter; \( C_{\text{root}} \) is the concentration of heavy metal in the root system, mg/kg of absolute dry matter [10].

For all studied plants, the coefficients are presented in table 8.
Table 8. Coefficients of biological accumulation and translocation factors for the studied plants.

| Plant species       | Cu CBN | Cu TF | Zn CBN | Zn TF | Mn CBN | Mn TF |
|---------------------|--------|-------|--------|-------|--------|-------|
| Bedstraw            | 7.5    | 2.5   | 39.0   | 2.5   | 4.0    | 1.2   |
| Cow vetch           | 19.5   | 0.4   | 9.9    | 0.1   | 15.9   | 0.8   |
| Field daisy         | 2.7    | 1.3   | 10.8   | 1.2   | 10.9   | 1.2   |
| Silverweed cinquefoil | 5.8  | 3.0   | 1.3    | 3.1   | 9.8    | 0.6   |
| Base vervain        | 25.1   | 0.1   | 71.7   | 11.0  | 11.6   | 15.0  |
| Winter cress        | 6.4    | 1.3   | 1.7    | 0.3   | 3.3    | 6.2   |

According to [10], if the coefficient of biological accumulation is greater than 10, then this type of plant can be attributed to a strong accumulator of this metal. If the coefficient of biological accumulation is in the range from 1 to 10, then this type of plant can be attributed to the average accumulator of this metal, if the coefficient of biological accumulation is less than 1, then this type of plant can be attributed to a weak accumulator of this metal.

4. Conclusion

Based on the obtained experimental data, we can conclude that of all the studied plants for the studied metals, only the bedstraw can be called a universal phytoremediation plant, although it has a relatively low coefficient of biological accumulation in copper and manganese. However, the values of the translocation factor for all metals exceeding one, allow for the use of the biomass of this plant as micronutrient fertilizers for soils that lack in copper, zinc and manganese.

In the absence of significant sludge contamination with copper, it is most preferable to use base vervain, which has the highest biological accumulation coefficient and translocation factor.

Thus, it is possible to select plants for artificial planting on sludge beds in order to further use these sludge beds as fertile lands.

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