Abstract

Emission of pollutants, including heavy metals, has a negative impact on the quality of soil. Remediation methods can be used to reduce the environmental impact of heavy metal contamination in soil by removing the pollutants themselves and by improving the quality of the soil.

Soil washing is one of the remediation methods used to remove heavy metals from the soil permanently. The quality of the washed soil, however, depends largely on the washing agent used. The main disadvantage of using conventional washing agents (e.g acid solutions, complexing agents), despite their high efficiency, is the damage caused to soil nutrients that determine its quality. Alternative washing agents are being sought in order to enable effective remediation with the simultaneous enrichment of the soil with macro- and micronutrients important for the further use of the soil.

The aim of the dissertation is to determine the effectiveness of washing agents, derived from municipal sewage sludge, for washing soils contaminated with Cd and a mixture of Cu, Pb and Zn, and to determine the physiochemical properties of the soil after remediation. The study was conducted in 3 stages: i) extraction and characterization of washing agents, ii) remediation of soils contaminated with heavy metals by washing under static and dynamic conditions, and iii) assessment of soil quality after remediation.

The washing was applied to soils with different physico-chemical properties, including texture (sandy loam, sandy clay loam, clay), organic matter content and sorption capacity. The soils contained heavy metals in concentrations typical for heavily contaminated sites (Cd 300 mg/kg, Cu 7874 mg/kg, Pb 1414 mg/kg, Zn 566 mg/kg).

Municipal sewage sludge is an important source of dissolved organic matter (DOM), humic-like substances (HLS) and humic substances (SHS). It has been shown that washing agents extracted from sewage sludge have adequate properties for the sustainable remediation of heavy metal contaminated soils. This is mainly due to the presence of functional groups (especially carboxylic groups) capable of complexing metal ions, the ability to reduce the surface tension of water, the presence of organic compounds enabling soil enrichment in organic matter and high concentrations of macronutrients (e.g. N, P, Ca, Mg). The washing agents obtained from sewage sludge do not cause secondary metal pollution as the extraction conditions prevent the heavy metals in the sludge from leaching into the washing agents.

Soil remediation was carried out under static and dynamic conditions (in a column reactor). Under static conditions, the efficiency of Cd and Cu, Pb and Zn removal was determined by type of washing agent, pH, washing time and number of washings. Under dynamic conditions, the effectiveness of remediation was analyzed depending on the type and flow rate of washing agents in the column reactor.

It has been shown that all washing agents tested in this study can be used for the remediation of soils heavily contaminated with heavy metals, but the effectiveness of the process depended on the type of washing agent, the type of metal the soil was contaminated with, and the washing conditions. Higher metal removal efficiency was achieved in static conditions. Under dynamic conditions, more effective metals removal from the soil was noted at a higher flow rate of washing agents, and regardless of the type of washing agent used, the effectiveness of remediation was impacted by the flow rate more than by the time with a stable flow rate in the reactor. The overall effectiveness of heavy metal elimination was determined by the efficiency of the removal of the heavy metals from the dominant chemical fractions, i.e. the reduction and ion exchange fractions for Cd and the ion exchange fraction for Cu, Pb and Zn. It has been shown that regardless of the washing conditions, DOM is effective in remediating soils heavily contaminated with Cu (efficiency 73-92%) and Cd (efficiency 68-87%), but not in soils contaminated with Pb (efficiency in the range of 5-24 %). Satisfactory Pb, Zn or Cd removal was obtained by using HLS (efficiency 65-90%) and SHS (efficiency 61-89%).

Remediation of soils with washing agents from sewage sludge resulted in enrichment of soils with organic matter. The highest increase in organic matter content was obtained by using the SHS solution, and the lowest by using the DOM solution. Similar trends were observed in the case of enrichment of the soil with humic substances (approx. 2-3 times increase in the soil after remediation with SHS). This is a favourable phenomenon considering the positive influence of humic substances on the properties and functions of the soil. Soil washing also increased the soil content of plant-available nitrogen ($N\text{-}NH_4$), phosphorus (P_2O_5) and potassium (K_2O) forms, but the level of increase of these macronutrients was impacted by the washing conditions (higher increase under static than dynamic conditions). The type of washing agent had a greater effect on the enrichment of soil with nitrogen than with phosphorus or potassium.

The obtained data showed that washing agents recovered from sewage sludge met the requirements of sustainable remediation. Their high efficiency in removing metals from heavily

contaminated soils (especially Cu and Cd), favorable impact on soil quality and low cost of acquisition make them an attractive alternative to commercial solutions.

The proposed remediation concept, consisting of washing/flushing the soil with washing agents obtained from sewage sludge is a part of the circular economy strategy in which waste (sewage sludge) is treated as a resource.