



# Sewage sludge can provide a washing agent for remediation of soil from a metallurgical area



Dorota Kulikowska, Barbara K. Klik\*, Zygmunt M. Gusiatin, Rafał Jabłoński

Department of Environmental Biotechnology, Faculty of Environmental Sciences, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland

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## ABSTRACT

The search for washing agents recovered from waste is a new trend in the washing of soils contaminated with heavy metals (HMs). In the present study, dissolved organic matter (DOM) recovered from sewage sludge was used to remediate soil that originated from a metallurgical area and was contaminated with Cu ( $8109 \text{ mg kg}^{-1}$ ), Pb ( $1473 \text{ mg kg}^{-1}$ ) and Zn ( $531 \text{ mg kg}^{-1}$ ). At pH 4 and a washing agent concentration of  $4 \text{ g TOC dm}^{-3}$ , HMs removal proceeded according to pseudo-second-order kinetics with a relatively short equilibrium time (120 min). DOM was especially effective for removing Cu; in double washing, Cu removal was  $5854 \text{ mg kg}^{-1}$  (process effectiveness 72%), Zn removal was  $258 \text{ mg kg}^{-1}$  (process effectiveness 50.5%), but Pb removal was low ( $131 \text{ mg kg}^{-1}$ ; 8.7%). DOM effectively removed metals from the exchangeable and acid soluble fraction. Based on the reduced partition index ( $I_R$ ), the intensity of Cu and Zn bonding in soil washed with DOM was twice as high as that in unwashed soil. Thus, DOM can serve as an effective washing agent for remediating soils contaminated with Cu and Zn, but it is not useful for removing Pb.

## 1. Introduction

The emission of heavy metals (HMs), a resulting of economic and technological development, pollutes the soil environment. In many countries, including Poland, the problem of soil metal pollution concerns mainly Cu, Pb and Zn. According to the Agency for Toxic Substances and Disease Registry among of 275 hazardous substances, Pb, Zn and Cu are at the 2nd, 75th and 118th positions, respectively (ATSDR, 2018). Thus, there is a need to protect soils and remediate polluted sites, which follows from the Thematic Strategy on Soil Protection and the Decision of the European Parliament and the Council (91386/2013/EU, 2013).

Among physicochemical remediation methods, only soil washing or soil flushing permanently removes metals from the soil. Soil washing employs physical processes (e.g. size separation) to separate the most contaminated soil particles, which in turn undergo chemical extraction with specific washing agents to transfer HMs from solid (the soil) to solution (Saponaro et al., 2002). The effectiveness of soil washing/soil flushing is influenced by many factors, including the type and properties of the soil, the concentration and solubility of the HMs and type of washing agents.

To increase the mobility of HMs, and thus the efficiency of soil remediation, numerous washing agents have been tested, including

various inorganic acids (Chen et al., 2015), organic acids (Gao et al., 2018; Merdoud et al., 2016; Song et al., 2015; Suanon et al., 2016) and complexing agents (Bolan et al., 2014; Niinae et al., 2008; Zhang et al., 2014). However, although these agents are effective at removing HMs from soil, they can alter soil properties in undesirable ways, e.g. washing out of nutrients (Jelusic and Lestan, 2015). Therefore, to optimize HMs removal in soil washing, the concentration of HMs in the washing solution after soil washing should be as high as possible, but without harming the soil/destroying soil composition. To achieve this, a number of natural agents were tested. It was shown that natural agents are attractive alternatives because they show great potential for HMs removal and tend to have fewer negative effects on soil properties. An example of such a natural agent is saponin, a plant biosurfactant, which is able to reduce surface and interfacial tension in water (Gusiatin, 2016). Unfortunately, plant biosurfactants are expensive, and their availability is limited, due to the fact that only a few plant species contain saponins at concentrations high enough to make their recovery profitable. Thus, searching for washing agents recovered from waste is a new trend in washing of soils contaminated with HMs. Washing agents should be compounds that have a high number of functional groups capable of forming complexes with metal ions and removing them from soil together with the washing solution. Such agents can be dissolved organic matter (DOM) of different origins, e.g. wastewater

\* Corresponding author.

E-mail address: [barbara.klik@uwm.edu.pl](mailto:barbara.klik@uwm.edu.pl) (B.K. Klik).

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treatment, food processing or wine processing.

DOC solutions prepared from wine-processing waste sludge efficiently removed Pb from contaminated soil (ca. 59% removal, initial Pb concentration in soil of 4920–5340 mg kg<sup>-1</sup>) (Chen et al., 2014). Although those authors used alkaline substances to prepare solutions of DOC, a high efficiency of Pb removal was dependent on low process reaction (pH 2–3). DOC solutions prepared from liquid fertilizer from food-waste composting were used to remediate Zn-contaminated soil (Zn concentrations up to 757 mg kg<sup>-1</sup> (subsoil) and 992 mg kg<sup>-1</sup> (topsoil) (Chiang et al., 2016). At 1500 mg dm<sup>-3</sup> DOC solution and pH 2.0, about 37% and 21% of the initial Zn was removed from topsoil and subsoil, respectively. However, soil washing with DOC at a higher pH of 3.0 was unsuccessful. According to the authors, proton replacement was likely to be the most important mechanism for Zn removal under low pH. When the soil was washed at a higher pH, the removal of Zn was dominated by chemical complexation with DOC, indicating that carboxylic and amide groups in DOC may be the major sites that interact with Zn<sup>2+</sup>.

The source of DOC can be sewage sludge, reached not only in humic substances but also poorly humified organic matter with low-molecular-weight organic fractions. Moreover, DOC can even be recovered from sewage sludge with elevated concentrations of HMs that would make the sludge unsuitable for agricultural use and composting. Based on our preliminary research, the HMs are not extracted from the sewage sludge when the washing agents are extracted (Klik et al., 2017). Thus, the use of these agents in remediation does not pose a risk of secondary soil pollution.

In this study, to remediate soil from a metallurgical area, DOM recovered from sewage sludge was used. The objectives of the study were i) to examine the effect of DOM concentration and pH on Cu, Pb and Zn removal efficiency, ii) to establish the kinetic parameters of the process, and iii) to determine Cu, Pb and Zn distribution and their binding intensity (as I<sub>R</sub> index) in soil before and after washing.

## 2. Materials and methods

### 2.1. Soil characteristic

Sampling site was located within former protection zone surrounding the Legnica smelter located in the central part of Lower Silesia Province, southwestern Poland. The soil samples were collected from topsoil layer (0–30 cm) in deforested terrain at site located at the distance of 70 m from the smelter. The soil was air-dried and ground to pass through a 2 mm sieve. The physicochemical characteristics of the soil are shown in Table 1. The soil was silt loam in texture, with a very low concentration of organic matter (OM) (0.44 ± 0.08%) and a pH close to neutral (6.8 ± 0.1). The dusts from the copper smelter were the main source of soil contamination with HMs. The concentrations of Cu and Pb were 8109 ± 31 mg kg<sup>-1</sup> and 1473 ± 18 mg kg<sup>-1</sup>, respectively, which exceeded the permissible values for industrial soils of 13.5-times and 2.5-times, respectively. The concentration of Zn was

**Table 1**  
Physicochemical characteristics of the soil.

Characteristic	Unit	Value ( ± SD)
Sand	%	25.6 ( ± 0.8)
Silt	%	67.0 ( ± 1.2)
Clay	%	7.3 ( ± 0.1)
Texture	–	Silt loam
Organic matter (OM)	%	0.44 ( ± 0.08)
CEC	cmol ( + ) kg <sup>-1</sup>	22.4 ( ± 0.7)
pH	–	6.8 ( ± 0.1)
Cu	mg kg <sup>-1</sup>	8109 ( ± 31)
Pb		1473 ( ± 18)
Zn		531 ( ± 11)

531 ± 11 mg kg<sup>-1</sup>, which was lower than the permissible value for this kind of soil (2000 mg kg<sup>-1</sup>). Cu, Zn, and Pb were in some heavy mineral phases. Cu forms mostly sulfides, chalcocite or chalcopyrite and also occurs in Fe-oxy-hydroxides or in secondary minerals. Zn occurs in irregular Fe-rich particles and forms phases such as gahnite, hemimorphite, and small inclusions of sphalerite. Pb-bearing phases comprise Pb silicate and metallic Pb in the form of small inclusions, as well as Cu and Cu-Fe sulfides. Secondary Pb phases include cerussite and hydroxypyromorphite (Tyska et al., 2016). In the contaminated soil, the fractionation of all metals (Cu, Pb, Zn) was determined (Section 3.4) in addition to the total metal concentrations.

### 2.2. Sewage sludge as a source of dissolved organic matter (DOM)

The source of the washing agent was sewage sludge after anaerobic fermentation, which came from a mechanical-biological municipal wastewater treatment plant (WWTP) located in Poland, with a capacity of 60,000 m<sup>3</sup> d<sup>-1</sup>. The sludge was dried and ground in a RETSCH SM-100 cutting mill (0.5 mm). The detailed characteristic of sewage sludge was presented in previous work (Gusiatin et al., 2017). Briefly, the sewage sludge had neutral pH (7.0 ± 0.1) and moisture on the level 83.2 ± 2.0%. The content of OM, total nitrogen and total phosphorus reached 71.3 ± 1.6%, 5.4 ± 0.3% and 2.0 ± 0.1%, respectively. Humic substances (HS) concentration was 227 ± 9.5 mg g<sup>-1</sup> OM, therein fulvic fraction (FF) and humic acids (HA) accounted 49% and 51% of HS. The concentrations of HMs in the sludge were below the permissible limits for sewage sludge in Poland.

The pH of the DOM solution was near neutral (6.8), which was due to the fact that water was used as an extractant. The original concentration of DOM in the extract (as TOC) was 6.8 g C dm<sup>-3</sup>, and the surface tension was 45.02 mN m<sup>-1</sup>. DOM contained the following concentrations of HMs (in mg dm<sup>-3</sup>): 1.1 (Cu), 0.0 (Pb), 0.7 (Zn).

### 2.3. Soil washing experiment

#### 2.3.1. Optimization of metal removal from soil by DOM

The soil washing experiments were conducted in batch conditions, in polyethylene tubes (50 mL) with a soil to DOM solution ratio of 1/40 (w/v). The samples were shaken in a mechanical shaker at 150 rpm at room temperature.

The suitability of the washing agent for removing HMs from soil was tested at different concentrations (as TOC): 1, 2, 3, 4, 5, 6, 6.8 g dm<sup>-3</sup>. Next, to establish the optimum pH, different pHs were tested (at the optimum concentration established in the previous step): 4, 5, 8, 9, 10. The pH of the washing solution was adjusted with HNO<sub>3</sub> and NaOH. After that, TOC was measured in the supernatants to determine the sorption of DOM. Next, to determine the optimum extraction time, soil was washed at the optimum concentration and pH for various time intervals (10, 30, 60, 120, 180, 240, 360, 480, 600 and 1440 min), after which samples were collected, centrifuged and filtered before Cu, Pb and Zn concentrations in the supernatants were measured. This allowed to determine the time needed to reach equilibrium and the kinetic constants of HMs removal.

#### 2.3.2. Single and double soil washing

For single and double soil washing, Cu, Pb and Zn removal from soil was conducted using a solution of DOM at optimal concentration, pH and washing time, as determined on the basis of the experiments described in Optimization of metal removal from soil by DOM. At the end of the extraction, the suspensions were centrifuged at 9000 rpm for 10 min and the supernatants were filtered. In the liquid samples, after both single and double washing, the total concentrations of HMs were measured. In the treated soils, the fractionation of HMs was determined after single and double washing. To estimate the stability of the HMs in the soil before and after washing with DOM, the reduced partition index (I<sub>R</sub>) was calculated for Cu, Pb and Zn. This index uses the results of a

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