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Microwave Enhanced Chromium Extraction from Sewage Sludge and Soil-Sludge Mixtures Using Biodegradable Chelants

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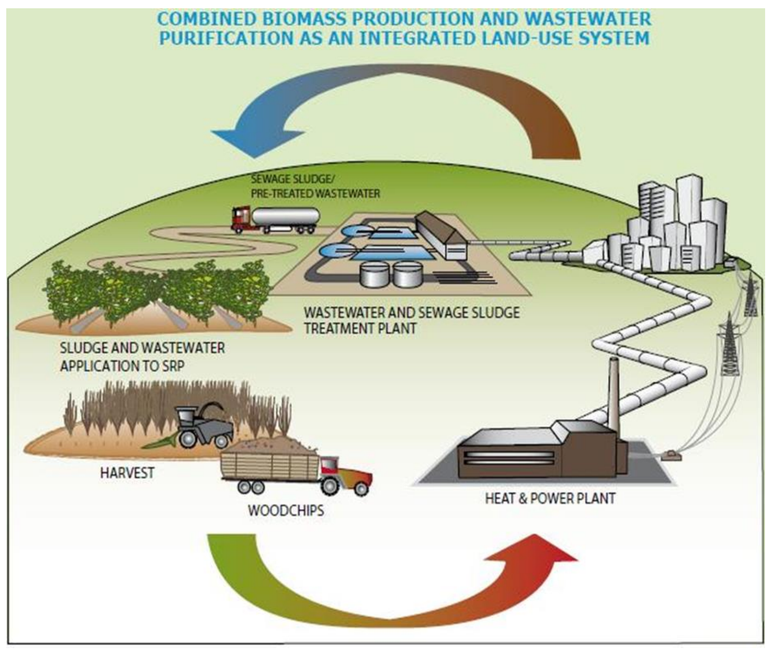
Introduction

Relevance of the research

It has been shown that sewage sludge (SS) on-land application improves physical, chemical as well as biological properties of the soil. SS can be a valuable source of plant nutrients such as nitrogen, phosphorus, calcium and magnesium also can act as an effective soil conditioner. However, safe SS utilisation is often limited by high content of heavy metals (HM), which can give rise to accumulation of these potentially toxic elements in the topsoil, following adverse effects on plant growth and crop quality. Moreover, SS on-land application poses a great concern because soil acts as a transferor, and due to bioaccumulation HM can appear in a food chain [1] [2].



Theoretical background

Negative impact of HM on the environment and human health can be effectively reduced by removing them from SS or soil-sludge mixtures. Various metal-extracting solvents can be used for chemical extraction: inorganic and organic acids, aqueous solutions of mineral salts, oxidizing or reducing agents, as well as organic chelate-type compounds that can form stable organic complexes with HM [3]. EDTA shows high effectiveness in removal metals from the solids, but unfortunately, due to its poor biodegradability, it is also very persistent in the environment. Therefore, investigators presume that EDTA is an unsuitable soil washing agent and stake on the use of more easily biodegradable ones. While, after HM removal soil-sludge mixtures could be finally utilised as a fertile growing media for fast growing plants in a biomass-biofuel-bioenergy chain.

The objective of the present study was to evaluate the efficiency of biodegradable chelating agents used for the microwave enhanced removal of Chromium (Cr) from SS and soil-SS mixtures, as well as to study the effect of pH on chelant-assisted washing at a different temperature range (50, 100, 150°C) and extraction duration (15 and 60 min).

References

1. Emmerich, W. E., Lund, J. L., Page, A. L. and Chang, A. C. (1982). Solid phase form of heavy metal in sewage sludge in sewage sludge treated soils. Journal of Environmental Quality. 11, pp. 178–181.
2. Praspaliauskas, M., Pedišius, N. (2017). A review of sludge characteristics in Lithuania's wastewater treatment plants and perspectives of its usage in thermal processes Renewable and Sustainable Energy Reviews 67:899-907.
3. Zaleckas, E., Paulauskas, V., Dainiene, R. (2007). Extraction of Cu from Sewage Sludge using Organic Acids // Rural development 2007. Kaunas-Akademija, 252-256.

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Methodology

Anaerobically digested SS was sampled at Kaunas wastewater treatment plant (WTP) after sludge dewatering. Chelant-induced HM removal experiment was carried out with strong metal chelating compounds (chelants) – organic aminopolycarboxyacids (Table 1).

Table 1. Chemical structure of chelating agents used as extractants for Chromium removal from sewage sludge

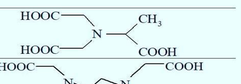
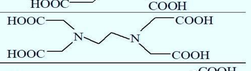
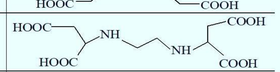
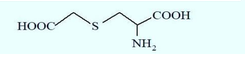
Extracting agent	Number of functional carboxygroups	Abbreviation	Chemical structure
Methyleneglycinediacetic acid	Tricarboxylic-	MGDA	
Ethylenediaminetetraacetic acid	Tetracarboxylic-	EDTA	
S, S'-ethylenediaminedisuccinic acid	Tetracarboxylic-	EDDS	
S-carboxyl-L-cysteine	Dicarboxylic-	SCLC	

Fig. 1. Main steps of batch experiments of heavy metal removal from sludge and sludge-soil mixtures

Removal tests have been carried out with SS and two different sludge-soil mixtures (mixture A – SS with clay soil; mixture B – SS with sandy soil). All chelating agents were used as 0.1M aqueous solutions, the pH was settled using NaOH or HNO_3, and extraction has been performed at a liquid/solid ratio – 10:1 and room temperature (20°C). Microwave-assisted HM extraction (at temperatures - 50, 100 and 150°C) was performed in the microwave A MLS–ETHOS (Leutkirch, Germany). Extraction was performed with 0.1M EDDS and MGDA solutions at a liquid/solid ratio 10, pH=6, extraction duration - 15 and 60 min. After extraction followed 25 min ventilation period, then solution was filtered and HM concentration in the solutions has been determined by AAS.

To study the effect of pH on chelant-assisted washing, the extraction experiments have been performed with the most promising chelating agents (0.1M EDDS and MGDA solutions) at different pH values in the range from 2 to 12, liquid/solid ratio 10, room temperature (20°C).

Results

Extraction results showed, that easier than EDTA biodegradable chelating agents, such as EDDS and MGDA, can be successfully used instead of widely applied metal-complexing agent EDTA, for chromium removal from sewage sludge as well as metal-contaminated soil. According to the complexation efficiency, the investigated chelants can be ranked in the following order: EDTA≈MGDA>EDDS>SCLC.

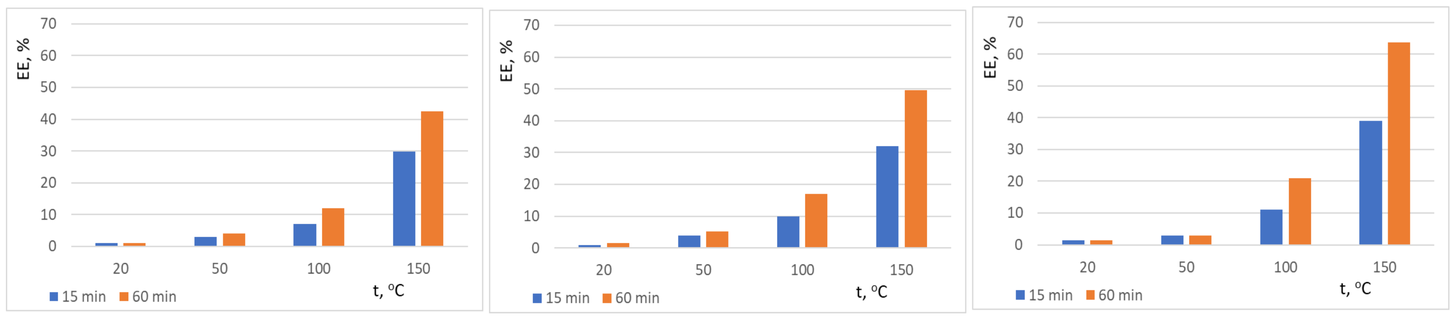


Fig. 2. Cr extraction efficiency dependency on temperature and duration – 15 and 60 min (0.1M MGDA, pH 6, solution/solid ratio – 10) from the solids: a- mixture A, b- mixture B, c- sewage sludge

Results showed (Fig.2) that elevated temperatures had particularly strong effect on Cr extraction efficiency from all the solids using MGDA chelant. The higher the temperature, the larger amount of metal was extracted – Cr EE from SS at 150°C after 1h was over 60%, while at 20-50°C EE did not exceed 10%. Generally, microwave extraction results were better, than the highest EE results achieved in batch-washing at room temperature. Similarly to batch washing, MW-assisted extraction efficiency from soil-sludge mixtures was also higher than that from sewage sludge.

Table 2. Chromium EE compared with extraction efficiency of the other HM

Chelant	Heavy metal	Temperature, °C	Max extraction efficiency, %	Extraction efficiency at 20°C, %
MGDA	Cr	150	64.0	1.7
	Cd	100	34.1	24.7
	Ni	100	57.6	25.9
	Pb	100	24.8	21.2
	Cu	50	12.6	22.8
	Zn	100	86.6	47.4

Results showed that according to their highest EE from SS applying MGDA heavy metals can be ranked in the following order: Zn>Cr>Ni>Cd>Pb>Cu for MGDA. It should be noted, that HM ranking order at room temperature was quite different.

Main conclusions

- Extraction results showed that readily biodegradable aminopolycarboxylic acids (such as EDDS or MGDA) had high metal removal capability from sewage sludge and sludge-soil mixtures.
- Chromium extraction efficiency using chelating agents increased with rising of solution temperature and with the decrease of pH of the extraction solution.
- According to the removal efficiency using MGDA Chromium was next after Zinc – the investigated HM according to their extraction efficiency from the solids with MGDA can be ranked in the following order: Zn> Cr> Ni> Cd> Pb> Cu .
- To summarize, the overall Chromium removal capacity of MGDA was better than that of EDDS.