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The effect of selected acidic or alkaline chemical agents amendment on leachability of selected heavy metals from sewage sludge☆

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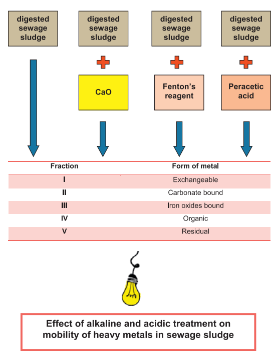
HIGHLIGHTS

- Pb, Cd and Ni fractions were analysed in chemically treated sewage sludge.
- Tessier fractionation method was used.
- Effect of alkaline (CaO) and acidic (Fenton's reagent or peracetic acid) treatment on metals' fractions was evaluated.
- Changes in mobility of Pb, Cd, and Ni in treated sludge were observed.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of the study was to evaluate the effect of acidic (Fenton's reagent, peracetic acid) or alkaline (CaO) chemical agents amendment on chemical forms of Pb, Ni, and Cd in sewage sludge. The dose of Fenton's reagent was as follows: $Fe^{2+} = 1\ g \cdot L^{-1}$, $Fe^{2+}/H_2O_2 = 1{:}100$; stabilisation lasted for 2 h. The dose of CaO was equal to 1 g $CaO \cdot g$ d.m.$^{-1}$. The dose of CH_3COOOH was 2.5 $g \cdot L^{-1}$. Total concentration of all metals in the digested sewage sludge was higher than in the soil and it did not meet Polish law requirements. Acidic chemical stabilisation of sludge did not significantly decrease total metal content in the sludge. Amendment of CaO decreased the content of Pb, Cd, and Ni in the sludge. Chemical fractions of heavy metals were identified in the sludge (exchangeable, carbonate bound, iron oxides bound, organic and residual). The results indicate that stabilisation of the sludge with Fenton's reagent and peracetic acid increased the exchangeable fraction of Pb, Cd, and Ni compared to the digested sludge, but it did not increase shares of mobile forms of metals considered as a total of I-st and II-nd fraction. Amendment of CaO increased percent share of examined metals in residual fraction. Not-mobile fractions of examined metals overweight the mobile ones in all sludge samples regardless of the treatment method.

1. Introduction

Digested sewage sludge contains macronutrients such as nitrogen, phosphorus, calcium, potassium, sodium, magnesium and other which are essential for plant growth. Because of this use of sewage sludge in agriculture or land reclamation is recommended as a method of its utilization. In 2015 in Poland, 568 thousand tonnes of sewage sludge was generated in municipal wastewater treatment plants. Among them, 126.6 thousand tonnes of dry solids were applied in agriculture. It means that only about 22% of stabilised municipal sewage sludge is discharged into the environment as a nutrient agent. In some European Union countries (e.g. in the Czech

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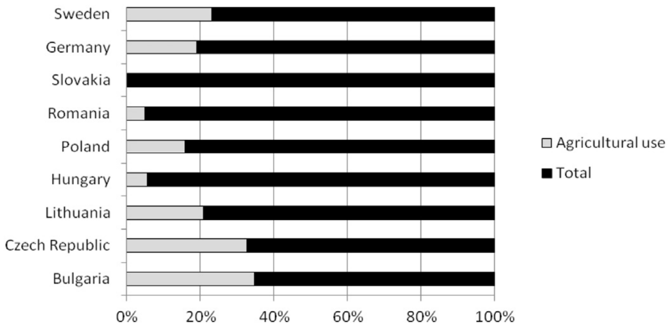

Fig. 1. Percent shares of agricultural use of sewage sludge in Poland and selected countries of former Eastern Block compared to selected "old" European Union countries (Inglezakis et al., 2014).

Republic and Bulgaria) this method of disposal is more frequently used than in Poland. In countries in which green economy is well developed (e.g. Sweden or Germany) the amount of sludge used in agriculture is comparable to that used in Poland (Fig. 1) (Inglezakis et al., 2014).

The main problem in the case of agricultural use of sewage sludge is contamination of this waste material with heavy metals (Bernacka et al., 2002). In Polish legislation, as well as in the European Union total concentration of heavy metals in sewage sludge is limited (Table 1). Also, data on the permissible values for United States legislation (Part 503) are given in Table 1. As can be seen from the data US limits for heavy metals concentration in sewage sludge are more liberal than the ones set by European Union. Polish standards are similar to the EU ones, however, there are some countries in the Union in which the standards for sewage sludge are much more stringent (Denmark, Finland, Sweden) or less stringent (Austria, Belgium, France, Germany). For example in Sweden permissible concentrations of heavy metals are as follows: Hg 2.5 mg·kg d.m.$^{-1}$, Cd 2 mg·kg d.m.$^{-1}$, Ni 50 mg·kg d.m.$^{-1}$, Cr 100 mg·kg d.m.$^{-1}$, Pb 100 mg·kg d.m.$^{-1}$, Cu 600 mg·kg d.m.$^{-1}$ and Zn 800 mg·kg d.m.$^{-1}$. Whereas in the Netherlands the limit values are even more restrictive and they are equal to Hg 0.75 mg·kg d.m.$^{-1}$, Cd 1.25 mg·kg d.m.$^{-1}$,Ni 30 mg·kg d.m.$^{-1}$, Cu 75 mg·kg d.m.$^{-1}$, Pb 100 mg·kg d.m.$^{-1}$ and Zn 300 mg·kg d.m.$^{-1}$ (Inglezakis et al., 2014).

The second limitation of sewage sludge use in agriculture in several countries is a presence of pathogens. In Poland, sludge cannot be used in agriculture if it contains *Salmonella*. In Finland *Salmonella* cannot be detected in a sample of 25 g of sewage sludge, whereas in France permissible content of *Salmonella* is 8 MPN per 10 g DM and in Italy, maximum content is 1000 MPN per 1 g DM. The legislation also includes other pathogenic organisms. In Poland limit for streptococci has been established (<100 per 1 g DM). In France, in sewage sludge which is used in agriculture limits for enteroviruses (3 MPCN/10 g DM) and helminths eggs (3/10 g DM) were set. In Hungary, other criteria were introduced. Faecal coli and faecal streptococci decrease below 10% of original number must be obtained (Inglezakis et al., 2014).

The concentration of heavy metals in sewage sludge depends first of all on the type of wastewater discharged into sewer system (municipal, industrial). It can vary a lot between different municipal wastewater treatment plants, but it can also fluctuate during a year According to the data given by Inglezakis et al. the differences in individual compounds concentrations can be >100% (Inglezakis et al., 2014). Also García-Delgado et al. indicate that concentrations of heavy metals in sewage sludge can vary significantly between the seasons and over the years (García-Delgado et al., 2007). The authors have observed significant differences between distribution fractions of metals considered together at different years for each individual metal. They have also observed variations in distribution of heavy metals' fractions of sludge collected at different times and seasonal periods. Spanos et al. have however observed that for the domestic-related metals (such as Zn, Pb and Cu the variability of concentrations in sewage sludge is low to moderate. High variability was observed in the case of the metals which presence in the sludge results mainly from industrial activities (Ni, Cd and Cr). For some elements it is possible to observe seasonal patterns (Spanos et al., 2016).

Important observations were made by Roig et al. They have stated that there is not visible correlation between heavy metal total burden and ecotoxicity of sewage sludge (Roig et al., 2012). The authors also emphasised that type of sewage sludge stabilisation might have a greater influence on ecotoxicity of the sludge than the load of pollutants. Singh and Agrawal observed that bioavailability of metals increases in sludge amended soil at excessive rates of application for many years (Sigh and Agrawal, 2008).

Particular attention must be given to the pollution of sewage sludge with the toxic heavy metals. The most toxic ones are lead, cadmium and nickel.

IARC classifies lead in class 2B (possibly carcinogenic for humans). It is rapidly taken up to the blood and soft tissues of human and animals' body. In a human body it is distributed into the bones. Moreover lead can inhibit enzymes, but particularly this metal affects a central nervous system. It was also shown that Pb affects synthesis of hemoglobin (at levels as low as 40 μg/dL) and caused damage of kidney (Heavy metals in waste, 2000). Total concentration of Pb in sewage sludge is in the range 13–26,000 mg·kg d.m.$^{-1}$ (Fytili and Zabaniotou, 2008). It is mainly bounded in sludge in residual fraction and adsorbed by Fe oxides and organic matter, it forms highly insoluble salts and complexes (Heavy metals in waste, 2000; Wilk and Gworek, 2009). Thus it is not well leachable and its exchangeability is rather low (Dabrowska, 2012). Intake of Pb in soil and sludge environment is affected by carbonates. Translocation of Pb in plants is limited and it is usually present at surfaces of roots and leaves. Reported toxic Pb effects to plants have been noted at concentrations in the range 100–1000 mg/kg soil (Heavy metals in waste, 2000).

Table 1
Permissible concentration of total heavy metals in sewage sludge according to the Polish, EU and US legislation (including proposed changes).

Legal act	Limit concentration [mg·kg d.m.$^{-1}$]						
	Hg	Cd	Ni	Cr	Pb	Cu	Zn
Polish decree of the Ministry of the Environment (Ordinance on sewage sludge, 2015)	16[1] 20[2] 25[3]	20[1] 25[2] 50[3]	300[1] 400[2] 500[3]	500[1] 1000[2] 2500[3]	750[1] 1000[2] 1500[3]	1000[1] 1200[2] 2000[3]	2500[1] 3500[2] 5000[3]
European Union law (Council Directve, 1986)	16 ÷ 25	20 ÷ 40	300 ÷ 400	no limited	750 ÷ 1200	1000 ÷ 1750	2500 ÷ 4000
New proposal for a directive, 2000 (Working document on sludge, 2000)	10	10	300	1000	750	1000	2500
New proposal for a directive, (Working Document on sludge and biowaste, 2010)	10	10	300	1000	500	1000	2500
United States legislation (Part 503) (Inglezakis et al., 2014)	57	85	420	3000	840	4300	7500

[1] In agriculture.
[2] For not agricultural purposes.
[3] For other purposes permitted by law acts.