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Extraction of heavy metals and phosphorus from sewage sludge ashes

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ABSTRACT

Phosphorus is a crucial element for food and fodder production, and generally for ecosystem stability. Phosphate fossil resources are its common source, but industry waste can be also a valuable alterative in agriculture applications. Sewage sludge, which comes from municipal wastewater treatment plants, is an important source of phosphorus, which is listed as a critical element for EU countries. Therefore, it is very important to implement new effective methods of phosphorus recovery from these type of waste into the fertilizer industry. It is available in large quantities in wastewater treatment plants, with biological stage based on activated sludge. However, municipal sewage sludge (MSS) contains significant amounts of various pollution types, including parasites, eggs, antibiotics, microplastic and heavy metals. Thermal conversion removes all organic matter, toxic organic compounds and all parasites, but increases concentrations of heavy metals. Different extraction methods of ash from thermal treatment of municipal sewage sludge enables the use of an effective, cheap, and simple technology of phosphorus recovery from sewage sludge ash through an easy soluble form of heavy metal removal. The aim of this work was to find a method for easy soluble forms of heavy metals removal to create an ash phosphorus fertilizer. It is therefore necessary to identify the amount of heavy metals and bioavailable phosphorus to determine the possibility of using sewage sludge ashes (SSA) as agriculture fertilizer. Experimental extraction with sulfur and acetic acid in different dilutions (0.05, 0.005, 0.0005 mol/dm^3 of H_2SO_4 and 0.001, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 mol/dm^3 of CH_3COOH) was introduced for bioavailable phosphorus and easy soluble forms of heavy metal removal to achieve safe levels of metal concentrations that fulfill requirements for mineral fertilizers. The obtained results show strong potential for phosphorus elution; however, a significant difference was observed in molybdenum removal compared to other heavy metals in acidic solutions.

Keywords: heavy metals, bioavailable phosphorus, sewage sludge, ash, extraction.

INTRODUCTION

Phosphorus is an essential element in agriculture, and the yield as well as plant health strongly depend on the occurrence of its water-soluble forms. In agricultural practice, phosphorus fertilizers made of phosphate rocks are widely used, but also organic fertilizers are an additional source of long-life phosphorus (Herzel et al., 2016). Ten-year forecasts for EU countries predict increased fertilizer consumption in many countries, especially Bulgaria, Slovakia, and Estonia. In this case, the global resources of phosphate rocks (estimated at 18 billion tons) will be depleted in 60 years (Franz, 2008). Therefore, new procedures or strategies are needed for industrial or agricultural use (Franz, 2008).

In the last century, organic fertilizers like cattle and pig manure or bird guano was used as a main source of phosphorus fertilization. The latter, which comes mainly from seabirds and pinnipeds or bats is extremely rich in organic matter and biogens, was introduced to the European market at a high price (Szpak et al., 2012). Due to the popularity of mineral fertilizer production, the overseas organic fertilizers role was depleted due to economic factors. Now, about 90% of fossil phosphorus sources of minerals are converted into phosphate fertilizers. Usage of phosphorus in one and multicomponent mineral fertilizers grow at a rate of 1.5–3.6% per annum (Spiak et al., 2022, Szaja, 2013). However, resources of phosphate-rich rocks are limited in mass and placed only in a few areas, so alternative sources of this precious element are strongly needed (van Vuuren et al. 2010).

Waste, like sewage sludge with high content of organic matter and phosphorus is also generated in large quantities in municipal wastewater treatment plants. The amount of dry mass of this type of waste exceeded in Poland 568,300 Mg in 2016 and 580,000 Mg in 2022. It has an average phosphorus content of about 3%, which gives over 17.000 Mg of pure phosphorus annually (Bień, 2012, Eurostat, 2024). This material is one of the most important phosphorus sources, creating potential agricultural use up to 19.000 Mg/a (Kruger et al., 2015, Regulation, 2019/1009).

It is important for agriculture sector, but the use of municipal sewage sludge (MSS) is most often limited by high content of toxic metals and also by the presence of persistent organic pollutants (POP), including antibiotics and endocrine active compounds as well as sometimes by the presence of living intestinal parasitic eggs (Iżewska & Wołoszyk, 2014, Poluszyńska & Ślęzak, 2015). There experiments to produce agricultural fertilizer from MSS, stabilizing sediments with fly ash from brown coal combustion, were conducted. However, the problem of high heavy metal content and polycyclic aromatic hydrocarbons (PAHs) that can be transferred from the agricultural soil into the food chain and finally to human body may limit its use in agriculture (Rosik-Dulewska et al., 2008, Rosik-Dulewska et al., 2016, Włodarczyk-Makuła et al., 2023). The possible is to reduce heavy metal levels and simultaneously save phosphorus in sewage sludge ash.

It is possible to use of solar energy for MSS drying, which creates high organic content material for energy recovery, e.g. in cement rotary kilns (Bień, 2012). A lot of common elements like Si, Fe, Al, Ca and P, can be found as a main component in SSA. On the other hand, it contains significant amounts of heavy metals – 9 to 13 times higher than in the raw MSS from which the ash was created. This phenomenon often precludes the use of this ash in agriculture due to law requirements (Guedes et al., 2016). However, SSA contains a significant amount of phosphorus, up to 11–13.4%, so it is ideal for recovery but heavy metals have to be removed before use (Ciesielczuk et al., 2016, Guedes et al., 2014). This problem was taken into consideration by the European SUSAN project, which aims to optimize the methods of biogen recovery from sewage sludge on the way to circular economy in parallel with minimizing the risk of soil contamination with heavy metals or persistent organic pollutants (Adam et al., 2009). A similar situation is present in the case of bottom sediments use. This material, originating from water reservoirs (dam reservoirs and lakes) and rivers, contains significant amounts of heavy metals. Thermal processes open new possibilities for phosphorus recovery, in case of its bioavailability (Strzebońska et al., 2015). The aim of this study was to remove easily soluble forms of heavy metals to improve the quality of sewage sludge ash as a potential phosphorus fertilizer.

PHOSPHORUS CONTENT AND FORM

After wastewater treatment with nitrification and denitrification processes based on activated sludge, generated sewage sludge all shares similar composition; however, in industrial wastewater and other specific wastewater types, phosphorus content can differ.

While the main component in sewage sludge ash (SSA) due to XRD and XRF analysis is quartz (about 20–30%), the content of phosphorus-rich compound whitlockite (CAS: 14358-97-5 $Ca_9(Mg,Fe)(PO_4)_6PO_3OH$), is also significant at 22%. Other phosphate compounds are also present, but in much lower quantities (Kasina et al., 2019). Due to the co-presence of Ca and Fe in this compound, elution in low pH can be lower than in the cases of Ca-P bounds predomination, like in Swiss SSA where iron oxide phosphate – $Fe_4(PO_4)_2O$ was found as a main phosphorus compound (El Wali, 2021, Huang et al., 2015).

The ash obtained from high temperature incineration of MSS is an rich source of phosphorus, and available in rising quantities. First sequential method was published by Golterman, but it was not dedicated to highly alkaline materials (Golterman, 1996). In the case of all bioavailable phosphorus extraction, there are several possible and economically justified methods.

Phosphoric acid extraction is one of widely suggested method of it recovery, but the pH value is indicated as significant, regardless of the type of acid used (Ciesielczuk et al., 2028). The probable reaction of recovery process with phosphoric acid is shown in the following equation (Weigand et al., 2013):

$$Ca_4Mg_5(PO_4)_6 + 12H_3PO_4 + 2H_2O = 4Ca(H_2PO_4) +_2 + 5Mg(H_2PO_4)_2 + 12H_2O \quad (1)$$

This, however, is still loaded with excessive amounts of heavy metals. Additionally, the highest degree of phosphorus leaching was obtained for the ash/acid ratio in the range of 0.33–0.49 (m/m). Properly obtained extract can be purified using acidic ion exchange resins. However, the content of metals in ash from sewage sludge is similar to that of metal ion contamination in phosphate ores exploited around the world, excluding zinc and copper (Weigand et al., 2013).

Whitlockite, a major phosphorus source, is enriched with hematite microcrystals, which are implemented into its crystalline structure. This specific conglomerate is a result of high temperatures during the combustion process, which favor the creation of semi-pure whitlockite, not crystals where iron atoms replace calcium in the whitlockite structure. Thus, the conditions of thermal treatment play a crucial role for effectiveness of phosphorus extraction process, because high content of iron can reduce the phosphorus recovery rate (Kasina et al., 2023).

MATERIALS AND METHODS

Pre-test

Four different ratios (S/L) – 1:10, 1:25, 1:50 and 1:100 – of 0.1 mol/dm^3 acetic acid to SSA were tested, due to acid consumption analysis during first two hours of extraction. The experiment was conducted in plastic containers at 25 °C. The pH value was measured using an Elmetron electronic pH-meter after 15, 30, 60, and 120 min.

Main test

The research material (SSA) comprised ashes from thermal treatment of MSS, which came from an industrial incineration plant. The ash was obtained by burning sewage sludge at 850 °C in the municipal c incineration plant in Nowiny, Poland.

In the tested SSA, the following parameters were measured: pH, electrolytic conductivity using the potentiometric methods, and organic matter content using the weight method. The content of macroelements like silicon, calcium, sodium, phosphorus, and potassium was determined using the XRF method and a Niton XL5 analyzer. The total content of investigated microelements was determined using an ICP-MS analyzer after microwave-assisted wet mineralization in aqua regia.

To assess optimal conditions for heavy metal extraction, different concentrations of sulfur (0.05, 0.005 and 0.0005 mol/dm^3) and acetic acid (0.001, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 mol/dm^3) were used. The control sample was extracted with deionized water with pH 8.24. Extraction was conducted in plastic containers through 24 hours of continuous shaking at room temperature with liquid/solid (L/S) 50:1 (v/m) ash: acid (or water) ratio (Karlfeldt-Fedje et al., 2010). The extraction ratio was established after pH pre-test III with 0.1 mol/dm^3 acetic acid. The obtained extracts were filtered through hard filters and analyzed using an ICP-MS analyzer. For all extraction experiments, 3 independent replications were made. The arithmetic means of the obtained values were used for further calculations.

PRE-TEST RESULTS

In all tested S/L ratios, the obtained results show slow acid consumption; however, different ratios of SSA sample to acid affect the pH levels during extraction (Fig. 1). Acceptable pH conditions for heavy metal removal were observed at the ratio of 1:50. Finally, this ratio was used in all main test experiments.

Other experiments conducted with this SSA focused on phosphorus extraction, confirming pH stability. The solution buffered to pH 3.55 used in Egner-Rhiem method changed to 3.94 after 30 min and to 4.08 after 24 hours, which is comparable with S/L 1:50 shown on Figure 1 (Ciesielczuk et al., 2018).

RESULTS AND DISCUSSION

The general characteristics of the investigated sewage sludge ash samples are shown in Table 1. The tested ash from sewage sludge incineration was alkaline due to a high content of

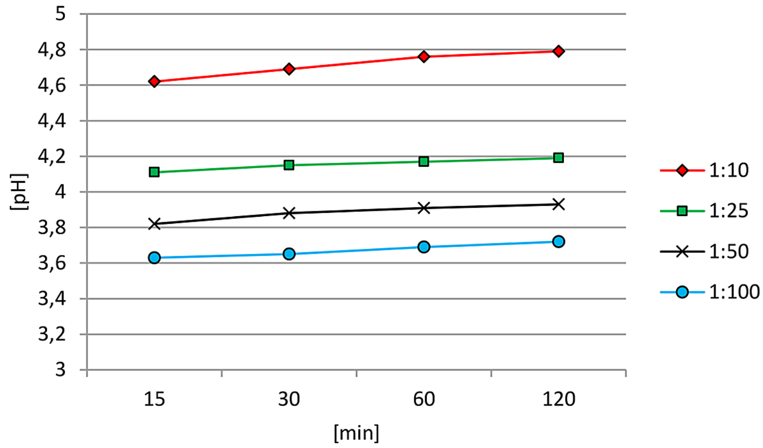

Figure 1. The pH levels and change for different (S/L) SSA to 0.1 mol/dm^3 acetic acid ratio

Table 1. Characteristic of sewage sludge ashes (SSA)

Parameter	pH $_{H2O}$	EC [mS/cm]	LOI [%]	CaO [%]	P_2O_5 [%]	Na_2O [g/kg]	K_2O [g/kg]
SSA	9.47–9.52	2.26	< 0.1	20.6	18.4	3.66	10.8
Ash(a)	12.44	3.23	0.15	22.8	30.7	7.57	-
Ash(b)	8.55	4.81	0.92	21.3	28.5	8.92	-
Ash(c)	-	-		22.8	21.0	4.8	6

Note: SSA – own results; Ash(a), Ash(b) – (Villen-Guzman et al., 2018); Ash(c) – (Franz, 2008).

alkaline elements, which is characteristic of this type of waste. The electrolytic conductivity of SSA was high (although the compared sludge ashes had much higher values); in the case of direct application as fertilizer, this could pose a threat to plant seedlings (Mazur et al., 2013, Ciesielczuk et al., 2017).

The share of main elements (Ca, Mg, K) was high, which is characteristic for the ashes from sewage sludge incineration, but the shares of Si and Fe are also high (Arnout &. Nagels, 2016, Franz, 2008), proving their value not only as a fertilizer but also as a replacement of lime for agriculture. High CaO content is a positive attribute, because CaO and P_2O_5 are the main components of SSA that react quantitatively with sulfuric acid and are thus major acid consumers. Other alkali oxides also react with SA, but leaching of Fe and Al compounds is present in low intensity (Franz 2008). In the investigated SSA, the Fe content is high at 9.981 g/kg dm, possibly indicating the presence of Fe-P compounds.

Original sewage sludge contains a significant amount of organic matter which mostly comprise nitrogen and phosphorus. This is important due to a predicted increase in phosphorus fertilizers use up to 2029. However, large differences in plant-available phosphorus quantities were found between similar wastewater treatment plants (Czechowska-Kosacka, 2016, EU Report, 2019). Sewage sludge could be used as a donor of organic matter for water binding and soil structure improvement. If the heavy metal content meets legal requirements, it can be used as waste material for fertilizing soils. This addition increase its water absorption, and supply many elements, including macro- and micronutrients, in bioavailable forms (Rosik-Dulewska et al., 2016). Sewage sludge added to soil as a fertilizer or a soil improvement factor increases total phosphorus content but can inhibit P supply to plants due to high Al and Fe content (Bøen et al., 2013). Nevertheless, in many cases, after initial drying, the sewage sludge is subject to incineration In specialized incinerators. In some countries (Holland, Switzerland), all generated sediments are burned. At high temperatures (> 950 °C), significant amounts of heavy metals evaporate; therefore, this could enable agricultural SSA use (Herzel et al., 2016). However, SSA contains not only calcium, potassium, and phosphorus but also higher concentrations of metals – especially zinc, copper, chromium, and lead – than the sludge from which it was made (Table 2).

Table 2. Heavy metal content in SSA [mg/kg DM]

Elements	SSA	A1	A2	A3	Morocco phosphate rock deposits (Westfall et al. 2005)	SSA Law requirements for agriculture (Kruger et al. 2015)
Zn	3330	3335	4360	2372	-	5000
Cu	729	758	1660	1175	-	900
Cr	139.1	45.5	730	130	225	300
Ni	78	54.6	660	57	26	80
Pb	119.4	293	70	285	7	150
Cd	7.55	3.25	8	7	30	50
Mo	27.3	-	40	25	-	x

Note: – "no data", SSA – own results; A1 – (Villen-Guzman et al., 2018); A2 –(Prabhakar et al., 2021); A3 – (Benassi et al., 2019), x – no specified requirements.

Making the fertilizers industry more flexible and development of new methods would allow the improvement of phosphorus recovery technology (e.g. with low energy demand) and establishment of new law rules for companies investing in MSS processing (Hukari et al., 2016). After high-temperature sewage sludge incineration, there is no organic matter in obtained material, but the content of phosphorus-rich compounds increases and retains its own high level of bioavailability; therefore, this material is a valuable source of this element, equal to phosphate fertilizers. The attempts to wash out phosphorus from ash are carried out by strongly acidic extractants, but this material contains excessive heavy metals (Hukari et al., 2016). Literature data show that in SSA, the compounds with bioavailable phosphorus are present in relatively high amounts, constituting on average over 30% of the total phosphorus. This creates considerable opportunities to use SSA as agricultural soil improver or even fertilizer (Kruger, 2015). However, the investigated ash contained excessive toxic metals, precluding it from fertilizing purposes.

Phosphorus elution

Phosphorus was found as a labile compound, especially with SA as extracting agent. Typical compounds like citric acid (Krupa-Żuczek et al., 2012), magnesium chloride (Bøen et al., 2013), or even sodium bicarbonate which is recommended for alkaline soils (Olsen et al., 1954), can be used only for bioavailable phosphorus forms detection.

The lowest removal, 12.6%, was noted for 0.005 M/dm^3, and the highest, 18.0%, for 0.05 M/dm^3, showing that SA is an effective phosphorus leaching agent even in low concentrations (Fig. 2).

This is confirmed via the Golterman method where Fraction III with 0.5 M/dm^3 can elute over 50% of total phosphorus (Ciesieczuk et al., 2018). Much better results were obtained with AA solutions. 0.01 and 0.02 M/dm^3 gave extremely low reductions of 1.41 and 1.81%, respectively. Initial pH levels were medium, at 5.13 and 4.74, so extraction strength was low. These two solutions fulfilled the phosphorus save target. The highest reduction level, 8.8%, was obtained for AA 0.08

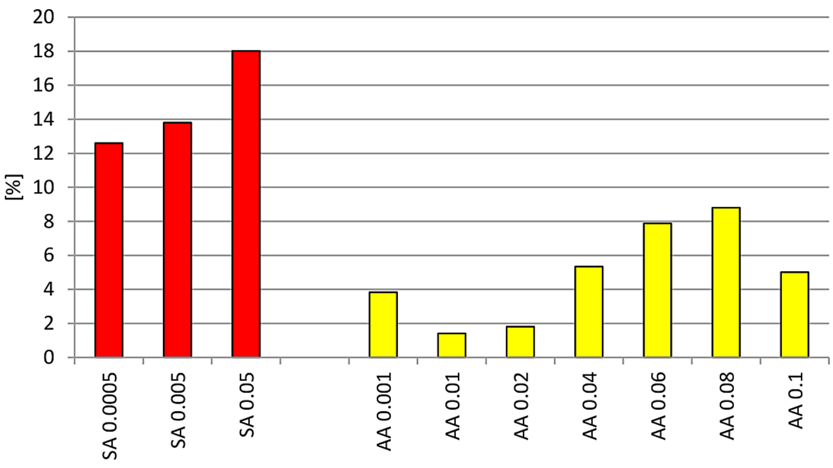

Figure 2. Reduction of phosphorus content in SSA after extraction

M/dm^3 and was parallel with the highest effectiveness of heavy metals reduction. This was still lower than levels noted with SA solutions.

Heavy metal removal

The highest content of metals was noted for zinc and copper, but the removal process was especially important for toxic elements like lead, nickel, chromium, and cadmium. Removal of heavy metals from ash was realized in two ways: with sulfur and with acetic acid.

One main factor in metal removal experiments is the pH of a solution. Low soluble compounds are more labile in low pH values, but the amount of acid used should be as low as possible. Deionized water was used as a control; in this case, pH was high, which is characteristic due to ash oxide composition (Fig. 3). In low concentrations of acids, pH was still high, and leaching action was weak.

The correlation factors calculated for SSA were very high – from 0.974 for Ni up to 0.999 for Pb. In the case of AA removal, characteristics were different, and correlation factors varied for each element from -0.589 for Cr to 0.531 for Cu.

The weakest extraction agent was water; obtained concentrations were low for all analyzed metals. The highest value, 0.403 mg/dm^3, was obtained for Cu. This is due to a high pH value controlled by Ca/S ratio. Richness in Ca material creates a high pH value, where leachability of elements usually does not exceed 0.1% of total content (Kasina et al., 2020). Therefore, water extraction results will not be discussed further.

Due to the AA and SA solutions used, different amounts of heavy metals were removed. In the samples obtained after extraction, significant quantities of Mo were removed, but other analyzed elements were more stable. Zinc is an essential element for plants, so its presence in the extracted SSA is valuable (Fig 4). Extraction with SA was much more effective than with AA, and there was not detected high leaching process in the wide pH range of 2–5 for AA (Yan et al.,

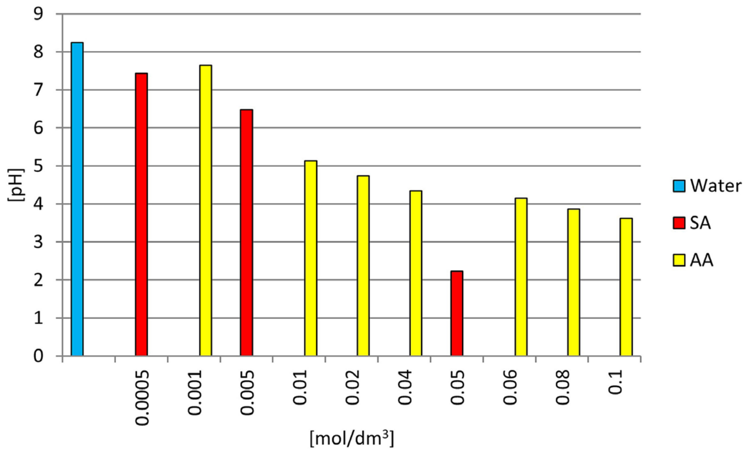

Figure 3. The pH values of solutions used in experiment

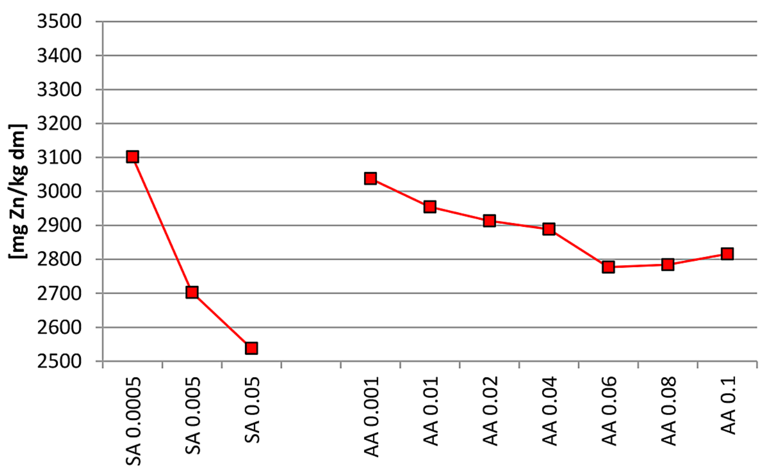

Figure 4. Content of Zn in SSA after extraction

2014). In terms of legal requirements, the highest concentration of SA (0.05 M) was optimal. At least 500 mg/kg was removed during extraction.

The results of Cu extraction were similar to those of Zn (Fig. 5). The best results were obtained with SA 0.05M, but leaching with AA also generated good results, with a final concentration of 638 mg/kg for 0.1 AA solution. The high correlation (0.95) of AA action for Zn and Cu curves confirms similar organic acid action in these two metals with different characters – more cationic (Zn) and amphoteric (Cu).

More toxic metals like Ni, Cr, and Pb were also effectively removed with 0.05 M SA, but AA action was weak (Fig. 6). Importantly, there was no correlation between pH of extraction medium and metals released. In this case, extraction with 0.1 M AA was no more effective than with 0.001 M. Due to the amphoteric character of Ni and PB, they could be removed from SSA even at high pH levels; however, this phenomenon was not observed.

Cadmium level is especially important for fertilizer quality. The highest reduction was obtained with 0.05M SA, but the difference between SA 0.005 and 0.5 M was only 1.16 g/kg of Cd (Fig.7). Low effectiveness of extraction shows a low bioavailability of Cd compounds. Acetic acid extraction did not correlate with acid concentration, but leaching results equal those obtained for SA 0.005 M use.

The reduction of metal concentrations obtained with sulfuric acid (SA) compared to total metal content is shown in Fig. 8. The behavior of heavy metals was similar for all analyzed elements. Reduction rate had positive correlation with acid concentration. Unfortunately, the highest reduction (38.3%) was observed in Mo, which is a necessary micronutrient for plants. Other metal reduction rates were lower, from 21.2% for Cd to 23.8% for Zn.

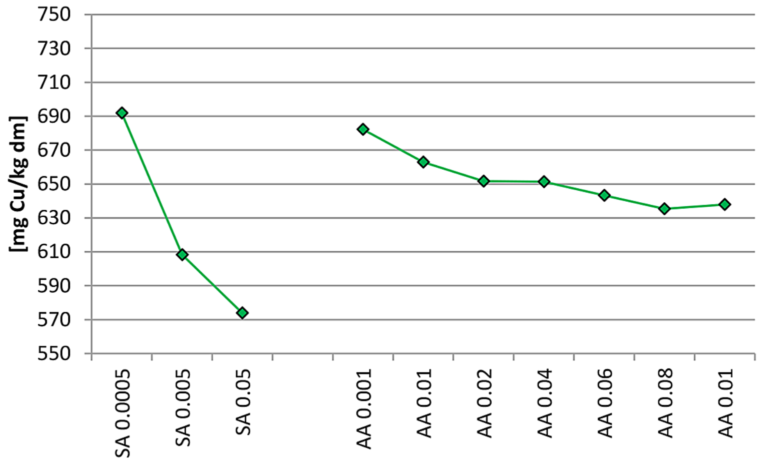

Figure 5. Content of Cu in SSA after extraction

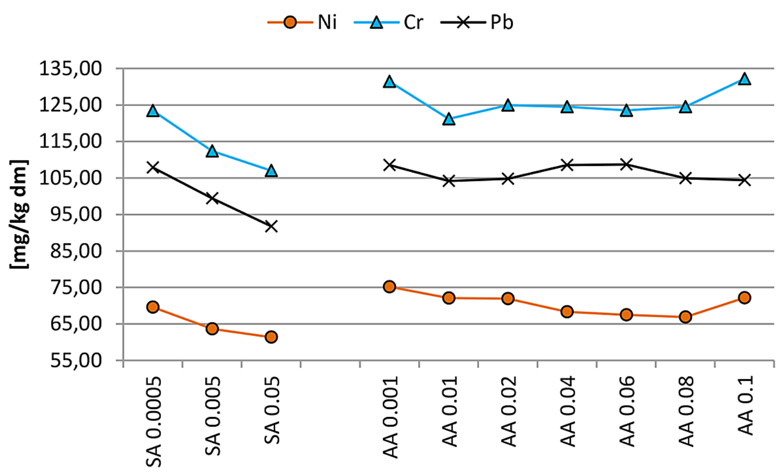

Figure 6. Content of Ni, Cr, Pb in SSA after extraction

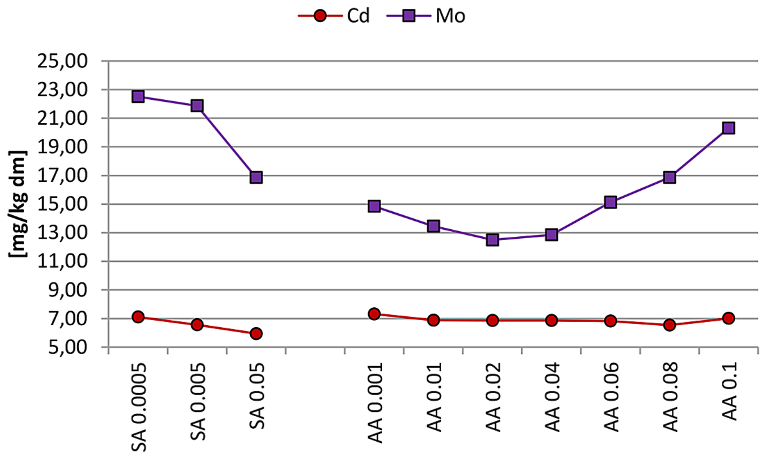

Figure 7. Content of Cd, Mo in SSA after extraction

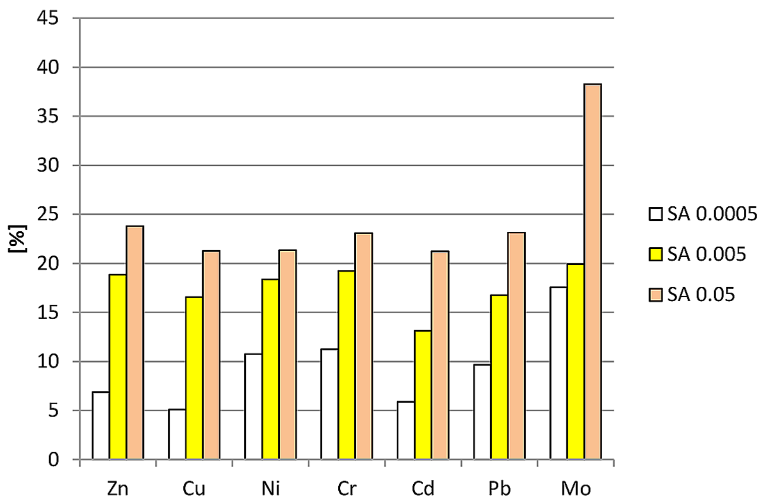

Figure 8. Reduction of metals concentration in SSA with sulfuric acid (SA)

The reduction of metal concentrations obtained with acetic acid (AA) compared to total metal content is shown in Figure 9. In sediment extractions at the same pH, organic acids showed stronger leaching ability than inorganic acids (Yan et al., 2014).

Other authors report high mobility of very stable and non-volatile Mo, where the solubility of Mo from SSA can exceed 86% of total content, with an average value of 40.9% (Nakić et al., 2017). Although the high temperature of MSS incineration demands high investment costs, it eliminates organic toxic components found in sludge (PAH, microplastic, drugs metabolites); at the same time, by mineralization of organic matter, it "enriches" the obtained material with phosphorus. After incineration, in SSA, the total phosphorus content can exceed 16.0%, but the share of plant-available compounds is dependent on process conditions and iron content (Guedes et al., 2016, Kasina et al., 2023). In raw municipal sewage sludge, before incineration, the total phosphorus share was reach only 2.97–6.64% (Poluszyńska & Ślęzak, 2015), while these values in the SSA examined here and obtained by other authors range between 13.8 and 18.4% (Ciesielczuk et al., 2018, Bezak-Mazur & Stoińska, 2013, Havukainen et al., 2016). Nowadays, a lot of good methods of phosphorus recovery have been developed, but removal heavy metals from SSA might be a better solution than use of high concentrated acids or high temperatures. This could be a way to save phosphorus forms practically available to plants (Weigand et al., 2013, Petzet & Peplinski, 2012, Shiba & Ntuli, 2016, Wzorek, 2008]. The new way forward, is to remove heavy metals and use SSA as fertilizer.

The challenge is finding a cheap reagent for heavy metal leaching. The chosen AA was weak, but this is very good for phosphorus content in extracted SSA.

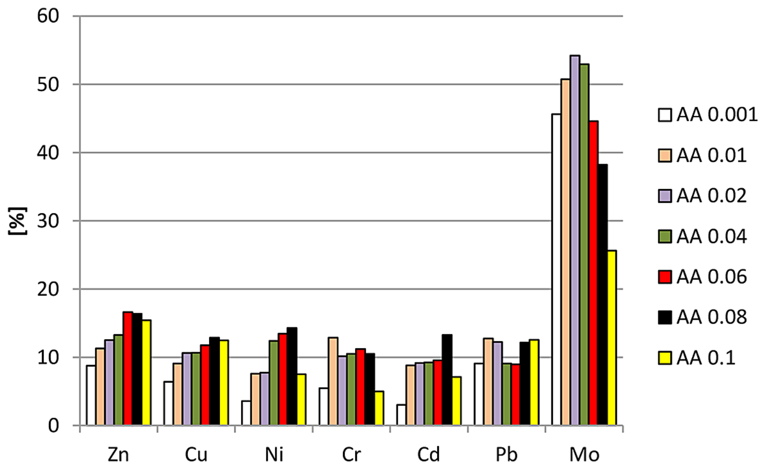

Figure 9. Reduction of metals concentration in SSA with acetic acid (AA)

CONCLUSIONS

The cheap and effective recovery of phosphorus from SSA material seems to be very effective, but the determination of the content of available phosphorus depends largely on the method used. The problem with using SSA in agriculture is the heavy metal content. Removing easily soluble heavy metal fractions makes it possible to achieve the metal levels required by law. In the tested ash samples, the most effective method of heavy metal removal was extraction with 0.05 mol/dm^3 sulfuric acid; however, in this case, significant amounts (18%) of phosphorus are also removed due to Ca-P bounds domination. The leaching of a significant amount of phosphorus does not predispose this method as good for producing fertilizer. Acetic acid was less effective, except for molybdenum, in heavy metal removal. However concentration of AA 0.8 mol/dm^3 has the highest potential for heavy metals removal, loss of phosphorus (8.8%) is too high. The optimal concentration for this process is 0.02 mol/dm^3 due to low phosphorus leaching (under 2%) and moderate strength in heavy metal mobilization. It could be an ecological way to improve the quality of sewage sludge ash and use it as mineral fertilizer in agriculture.

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