INTERNATIONAL JOURNAL
OF
CONSERVATION SCIENCE
ISSN: 2067-533X Volume 12, Special Issue 1, August 2021: 765-780 www.ijcs.ro

INFLUENCE OF FLY ASH ADDITION ON THE IMMOBILISATION OF HEAVY METALS IN SEWAGE SLUDGE

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Abstract

Municipal sewage sludge is characterized by high soil forming and fertilizing potential. Therefore, the use of sewage sludge for soil fertilization seems the most efficient method of its disposal because valuable biogenic elements, such as: N, P, Mg or K, are reintroduced to the soil. But, the waste product from wastewater treatment plant, except for valuable elements, can contain also hazardous substances, e.g. heavy metals which can limit land use of the sludge.
Fly ash generated from the lignite combustion is categorized as high-calcium ash, and for this reason it may be used for stabilization and immobilization of heavy metals in sewage sludge, instead of calcium oxide. The paper presents the results of the laboratory study on the influence of adding the fly ash, generated during the lignite combustion, to municipal sewage sludge (in doses 0 to 1kg/kg d.m.) and the reaction time (directly after mixing, after 14 and 28 days), on the chemical transformations and mobility of heavy metals in sewage sludge. The results showed that fly ash addition increased the percentage of the low mobile fractions of the metals.

Keywords*: Sewage sludge management, Fly ashes, Mobility of heavy metals, Soil and water protection*

Introduction

Sewage sludge is an inseparable byproduct of wastewater treatment process. The methods of sewage sludge management have largely been determined by the legal regulations regarding the quality of wastewater discharged from wastewater treatment plants to the receiving waters [1].

Increasingly stricter regulations introduced in many countries [2, 3] prohibit the sewage sludge storage at landfill sites. Due to the above, the sludge management sector faces serious economic, technical and ecological problems that need to be solved.

Until recently, the final stage of sewage sludge disposal was its mechanical dewatering and further on, drying and depositing at landfill sites. Currently, the new regulations lead up to:

- the total ban on sewage sludge landfilling;
- the increase in application of thermal methods in sludge management;
- the increase of the volume of the processed municipal sewage sludge before its introduction into the environment, the maximization of the degree of the use of biogenic substances contained in sludge, while meeting the requirements regarding the sanitary, chemical and environmental safety [4].

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In Poland, in 2010-2018, the greatest amount of produced sewage sludge was subjected to incineration. A declining trend was observed in relation to the landfilling of sludge as well as its application in plant cultivation, for compost production, and land reclamation. In the case of its application in agriculture, no significant changes were observed in the considered period (Fig. 1).

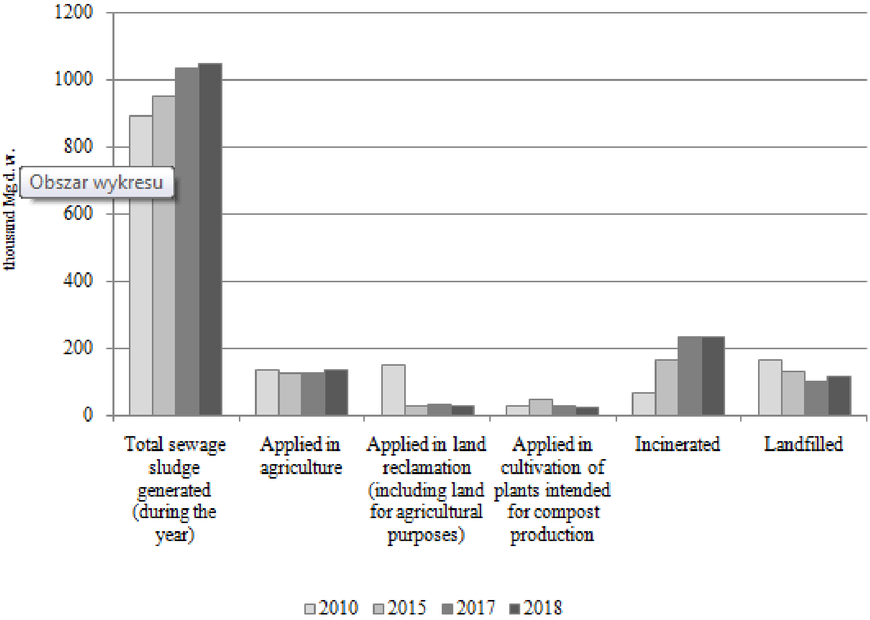

Fig. 1. Sewage sludge management in Poland in the period from 2010 to 2018 [5]

The sewage sludge generated in wastewater treatment plants has a high fertilizing potential and can be used in agriculture or land reclamation, when the concentrations of heavy metals do not exceed the permissible values [6, 7].

The presence of heavy metals in sewage sludge and especially their high concentrations results mainly from the presence of industrial wastewater in the overall wastewater stream. But, the heavy metals contained in municipal wastewater can originate from household sewage, surface runoffs or corrosion processes.

The main heavy metals that have the most harmful effect on living organisms are: lead, cadmium, nickel and chromium. Except for nickel, the heavy metals enumerated above are highly susceptible to bioaccumulation. Copper and zinc (microelements) are essential for proper plant growth but when highly concentrated, they adversely affect the living organisms [8].

The concentration of heavy metals in sewage sludge is also important when it comes to landfilling due to the risk of their leaching and a possibility of penetration into the soil and aquifers. In the case of the storage of the residues from the sewage sludge incineration process, their concentration increases several times as compared to their concentration in the starting material [9-11]. Our knowledge concerning the total concentration of heavy metals does not reflect the potential hazard they may pose. The fractions of heavy metals that are soluble in water, the so-called exchangeable metals, and metals bound to carbonates are considered the most mobile. The heavy metals bound to iron and manganese oxides, as well as those bound to organic matter are also available for plants; however, their release into the soil is significantly slower [12, 13].

Over 90% of the area of Poland is covered by soils formed from sedimentary rocks transported by glaciers from Scandinavia. Due to the above, the majority of soils within the country is naturally strongly or moderately acidic with rather low water holding capacity, poor nutrient availability and low organic matter content. Thus, increase of pH of soils by addition of alkaline materials is very favourable process.

Sewage sludge is often conditioned by mixing with highly alkaline substance like a quick lime. Such sludge is effective deacidfier for the soils with low pH. But, fly ashes from lignite combustion that have high pH can be used instead of calcium compounds. One of the common methods of sewage sludge management which deserves particular attention is mixing it with fly ash in order to obtain two processes: solidification and stabilization of the sludge [12]. The additive of this type of material to the sewage sludge results in the removal of water from sludge and also in the change of its physical and chemical properties [13]. As a result, the consistency of sewage sludge is changed from liquid or semi-liquid to solid which makes it easier to transport the material to its destination point. The formation of the earth-like structure of sludge, as opposed to the sticky consisted obtained as a result of the additive of CaO, is the final effect of the process [14]. The transportation and application of the obtained sticky-consisted product is difficult. In the case of the CaO addition to the sewage sludge, instead of fly ash characterized by a high content of calcium, the final product that can cause intensified dusting, is obtained. Due to addition of calcium compounds and pH changes, the ions of heavy metals contained in sewage sludge are subjected to chemical transformation [15-18].

The application of CaO for the sewage sludge stabilization and dewatering has also other negative effects. The intensive course of the process resulting in the temperature increase contributes to the losses in the nitrogen content through ammonia volatilisation.

The use of fly ash from lignite combustion and sewage sludge at the same time can be considered as the cost effective waste disposal method.

The aim of the study was to assess the influence of the addition of fly ash produced during the lignite combustion into the municipal sewage sludge and the reaction time on chemical transformation and mobility of heavy metals in the sewage sludge.

Materials and methods

The study on the influence of fly ash addition on fate of heavy metals in sewage sludge was carried out on the sewage sludge derived from the municipal wastewater treatment plant in Lubartów and fly ash generated in the process of lignite combustion in Bełchatów Power Plant.

In the wastewater treatment plant in Lubartów, with the capacity of 5500m^3/d, aerobic stabilization of excess sludge in the process of extended activated sludge aeration is conducted. Thickening of aerobically stabilized sludge occurs in the thickener, which is continuously fed with excess sludge, directly from the activated sludge tank. The reception of thickened excess sludge is adjusted to the operation of the mechanical press, in which the final dewatering of sludge is performed.

In order to carry out chemical precipitation of phosphorus compounds, a coagulant – ferrous sulfate in the form of PIX product – is used. Over a single day, 25 tons of sewage sludge, with water content of approximately 82% and organic substance content of about 47% (dry mass), are produced.

The total concentrations of selected components in sewage sludge and fly ash used in the experiment are presented in Tables 1 and 2.

To assess the influence of fly ash addition on the conversion of heavy metals chemical forms, the leaching tests were performed on sewage sludge and sludge-ash mixtures. The analyses were carried out three times: immediately after the experiment was started, after 14 and 28 days of the test. The samples of each material taken into the analysis were dried for 48 hours at a temperature of 105^{o}C and next, the dried materials were ground in a ball-grinder to obtain the homogenized samples. The total content of carbon (TOC) in the samples was determined by using TOC analyzer (SSM 5000A Shimadzu), and pH value was measured potentiometrically with using pH meter (CPC-505 ELMENTRON).

Table 1. Heavy metals content in municipal sewage sludge

Metal	Sewage sludge				
	IV 2018	X 2018	IV 2019	Average value	Standard deviation
	mg/·kg d.m				
Lead	23.08	24.06	24.15	23.76	0.59
Cadmium	2.57	2.54	2.49	2.53	0.04
Nickel	37.4	37.23	37.51	37.38	0.14
Zinc	232	232.5	235.22	233.24	1.73
Copper	48.02	46.1	50.01	48.04	1.96
Chromium	99.8	97.56	97.82	98.39	1.23

The following doses of fly ash were applied in the experiment: 0.2; 0.6; 1.0kg ash/kg d.m of sewage sludge. The sludge without the addition of ash was used as a control material.

Table 2. Chemical composition of fly ash from the Bełchatów Power Plant

Component		Unit	Fly ash [19]
Silica	SiO_2	[%]	11.35
Aluminum	Al_2O	[%]	4.66
Iron	Fe_2O	[%]	9.54
Calcium	CaO	[%]	50.02
Magnesium	MgO	[%]	7.92
Sodium	Na_2O	[%]	0.14
Potassium	K_2O	[%]	0.04
Lead		$mg \cdot kg\ d.m^{-1}$	30.69
Cadmium		$mg \cdot kg\ d.m^{-1}$	0.97
Nickel		$mg \cdot kg\ d.m^{-1}$	22.77
Zinc		$mg \cdot kg\ d.m^{-1}$	79.20
Copper		$mg \cdot kg\ d.m^{-1}$	23.20
Chromium		$mg \cdot kg\ d.m^{-1}$	136.00

The sequential extraction according to the Tessier procedure (Table 3) was carried out on these samples. After each stage of extraction the solid phase was separated from the liquid phase by means of centrifugation on the MPW-350 centrifuge (time of centrifugation – 30min, rotation speed – 4000rot/min). Next, the residual sample was rinsed with a small amount of distilled water which was then added to the formerly extracted solution.

The concentrations of heavy metals in the extracts and the final residuum were determined with the use of inductively coupled plasma atomic emission spectrometry (ICP JY 238 ULTRACE), after the mineralization of the samples in CEM-2100 microwave oven.

The research results presented in the tables below are a mean from three series of measurements.

Table 3. Scheme of analytic procedures in sequential extraction [20]

Fraction	Type of extracting agent	Temperature (°C)	Duration and conditions of extraction
I. Exchangeable metals	1M $MgCl_2$, pH=7	22	shaking 1h
II. Metals bound to carbonates	1M CH_3COONa acidified CH_3COOH, pH=5	22	shaking 5h
III. Metals bound to iron and manganese oxides	0,04M NH_2OH • HCl in 25% (v/v) CH_3COOH	95	shaking 5h
IV. Metals bound to organic matter	0,02M HNO_3 + 30% H_2O_2atpH=2	85	shaking 2h
	H_2O_2 , pH=2		shaking 3h
	3,2M CH_3COONH_4 in 20% HNO_3 (v/v)	22	shaking 0.5h
V. Metal residues	HF + HNO_3	Mineralization	

Results and discussion

Sewage sludge used in the experiment were characterized by many time lower values of heavy metals (Table 1) than the limit values given in the European Law for the sludge used in agriculture (86/278/EEC). Heavy metals content in ash was also low.

Concentrations of cadmium, zinc and copper and nickel in this material were lower comparable to the sludge. Only concentration lead and chromium was a little higher (Table 1).

The percentage of particular fraction of metals varied depending on type of the examined material. The results of the leaching tests which were conducted in the initial phase of the experiment and after 14 and 28 days of its duration are presented in Tables 4-6.

Table 4. Results of the speciation analysis of heavy metals content in sewage sludge and sludge-ash mixtures measured immediately after the experiment was started

Material	Fraction	Content of particular heavy metals (%)					
		Pb	**Cd**	**Ni**	**Zn**	**Cu**	**Cr**
Sewage sludge	I	3.15	12.25	9.20	7.10	0.52	1.60
	II	5.20	12.60	9.15	20.90	0.48	1.60
	III	18.82	27.10	36.50	50.56	0.50	22.90
	IV	29.41	17.35	26.20	7.90	88.21	53.10
	V	43.43	30.70	18.95	12.88	10.29	20.80
Sludge + fly ash in dose 0.2kg/kg d.m of sludge	I	2.80	12.49	12.35	5.33	3.80	10.92
	II	3.15	12.72	24.55	22.60	3.42	9.76
	III	21.35	19.62	13.21	52.69	1.80	34.02
	IV	28.30	17.15	17.45	5.10	82.45	38.40
	V	44.40	38.02	32.44	14.28	8.53	6.90
Sludge + fly ash in dose 0.6kg/kg d.m of sludge	I	2.45	13.50	9.13	5.70	7.80	6.15
	II	2.73	13.40	10.45	22.45	2.75	2.72
	III	22.16	18.21	33.10	53.60	1.53	32.10
	IV	26.40	16.21	16.21	4.90	77.14	36.80
	V	46.26	38.68	31.11	13.90	10.78	22.23
Sludge + fly ash in dose 1.0kg/kg d.m of sludge	I	1.82	14.20	8.23	6.45	9.20	2.10
	II	3.90	13.90	8.10	23.20	2.30	2.50
	III	24.40	19.02	22.73	54.10	1.92	27.10
	IV	20.60	14.21	15.20	4.35	61.45	26.45
	V	49.28	38.67	45.74	11.35	25.13	41.85

Table 5. Results of the speciation analysis of heavy metals content in sewage sludge and sludge-ash mixtures after 14 days of the experiment

Material	Fraction	Content of particular heavy metals (%)					
		Pb	**Cd**	**Ni**	**Zn**	**Cu**	**Cr**
Sewage sludge	I	5.10	15.92	11.90	4.90	2.85	1.54
	II	3.54	15.73	11.29	8.90	2.03	1.62
	III	23.76	13.49	33.15	29.55	0.91	32.01
	IV	25.36	10.60	23.16	7.90	50.21	38.21
	V	42.24	44.26	20.50	48.75	44.00	26.62
Sludge + fly ash in dose 0.2kg/kg d.m of sludge	I	1.62	7.62	15.33	11.81	4.92	13.02
	II	2.65	8.42	20.55	15.21	4.16	11.65
	III	18.22	19.03	12.35	51.76	1.59	17.60
	IV	25.36	10.25	9.73	3.12	14.65	25.30
	V	52.15	54.68	42.04	18.10	74.68	32.43
Sludge + fly ash in dose 0.6kg/kg d.m of sludge	I	1.22	7.62	11.98	7.70	8.75	8.40
	II	2.73	7.10	6.88	15.92	2.30	5.30
	III	20.10	18.65	31.55	52.45	1.34	15.21
	IV	20.92	10.42	8.44	2.40	11.25	22.12
	V	55.03	56.21	41.15	21.53	76.36	48.67
Sludge + fly ash in dose 1.0kg /kg d.m of sludge	I	1.25	7.62	10.02	8.50	10.30	5.02
	II	2.61	7.10	5.55	15.62	2.75	5.45
	III	23.55	18.65	21.82	54.10	1.60	14.50
	IV	12.61	9.21	7.65	2.50	6.10	19.22
	V	59.98	57.42	54.96	19.28	79.25	55.81

Table 6. Results of the speciation analysis of heavy metals content in sewage sludge and sludge-ash mixtures after 28 days of the experiment

Material	Fraction	Content of particular heavy metals (%)					
		Pb	**Cd**	**Ni**	**Zn**	**Cu**	**Cr**
Sewage sludge	I	7.85	17.05	12.06	3.53	4.19	1.48
	II	4.16	16.67	11.95	4.80	2.30	1.71
	III	24.31	11.42	31.19	26.40	0.80	19.92
	IV	25.36	7.30	19.45	3.50	44.21	21.50
	V	38.32	47.56	25.35	61.77	48.50	55.39
Sludge + fly ash in dose 0.2kg/kg d.m of sludge	I	1.12	4.70	16.85	12.26	5.43	13.92
	II	2.10	4.95	17.55	13.16	4.51	12.50
	III	14.12	18.50	11.82	49.68	1.50	11.60
	IV	19.28	6.90	6.30	2.53	11.35	21.45
	V	63.38	64.95	47.48	22.37	77.21	40.53
Sludge + fly ash in dose 0.6kg/kg d.m of sludge	I	0.95	3.52	13.20	8.60	9.26	9.72
	II	2.40	3.30	4.21	11.30	2.70	6.25
	III	16.21	16.96	30.45	51.95	1.26	9.20
	IV	16.20	5.70	5.00	2.02	10.28	18.60
	V	64.24	70.52	47.14	26.13	75.96	56.23
Sludge + fly ash in dose 1.0kg /kg d.m of sludge	I	1.95	3.20	11.52	9.73	10.82	6.10
	II	2.35	2.53	3.40	12.21	3.02	6.50
	III	19.92	18.16	21.45	53.58	1.65	8.92
	IV	7.60	5.12	4.72	1.89	7.62	11.20
	V	68.18	70.99	58.91	22.59	76.89	67.28

Graphical presentation of differences in particular metal fractions between the materials (sewage sludge and the sludge-ash mixture) determined at the beginning of the experiment is shown in Fig. 2, and time dependent changes in in percentage of particular fractions of the examined metals in the materials are shown in Figs. 2 and 3.

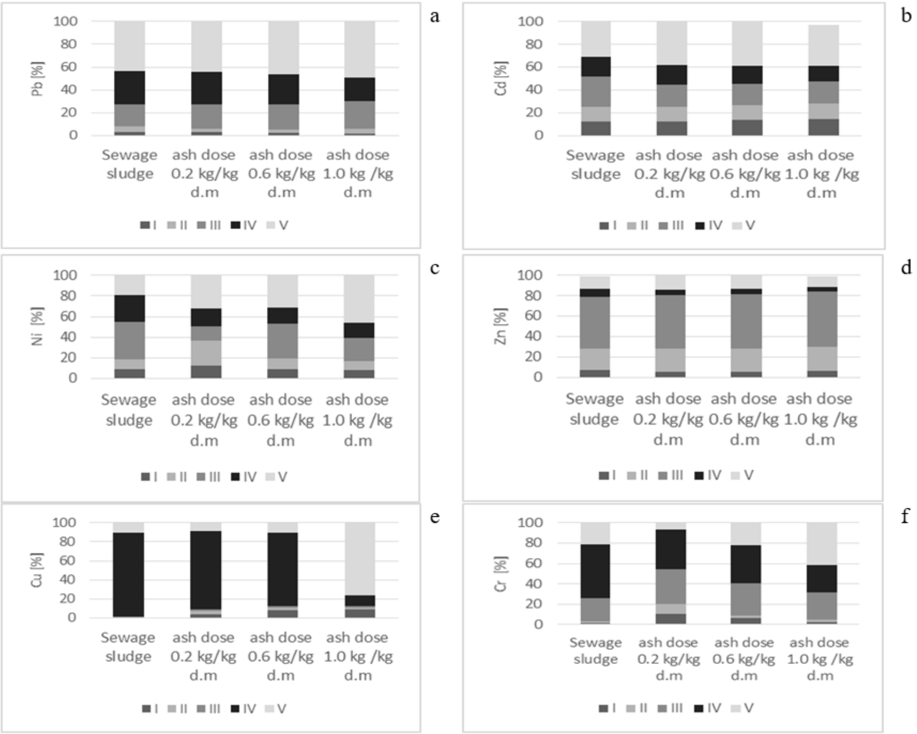

Fig. 2 Percentage of particular fraction of: a) lead, (b) cadmium, (c) nickel, (d) zinc, (e) copper and (f) chromium in sewage sludge and sludge-ash mixtures determined at the beginning of the experiment.

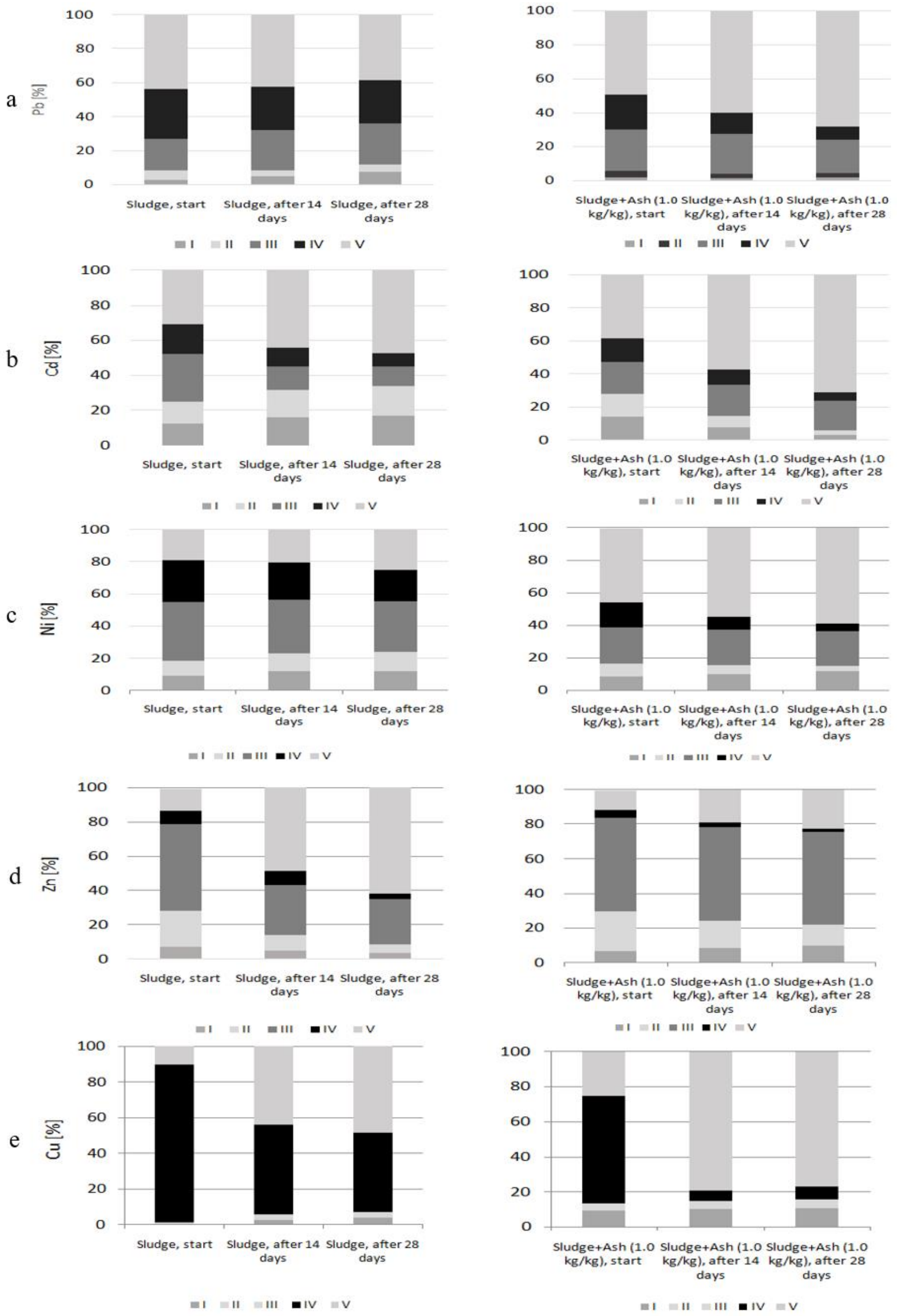

Fig. 3. Comparison of time dependent changes in percentage of particular fractions of lead: (a) lead, (b) cadmium, (c) nickel, and (d) zinc in sewage sludge and the mixture of sludge with the highest dose of fly ash; (e) copper and (f) chromium in sewage sludge and the mixture of sludge with the highest dose of fly ash

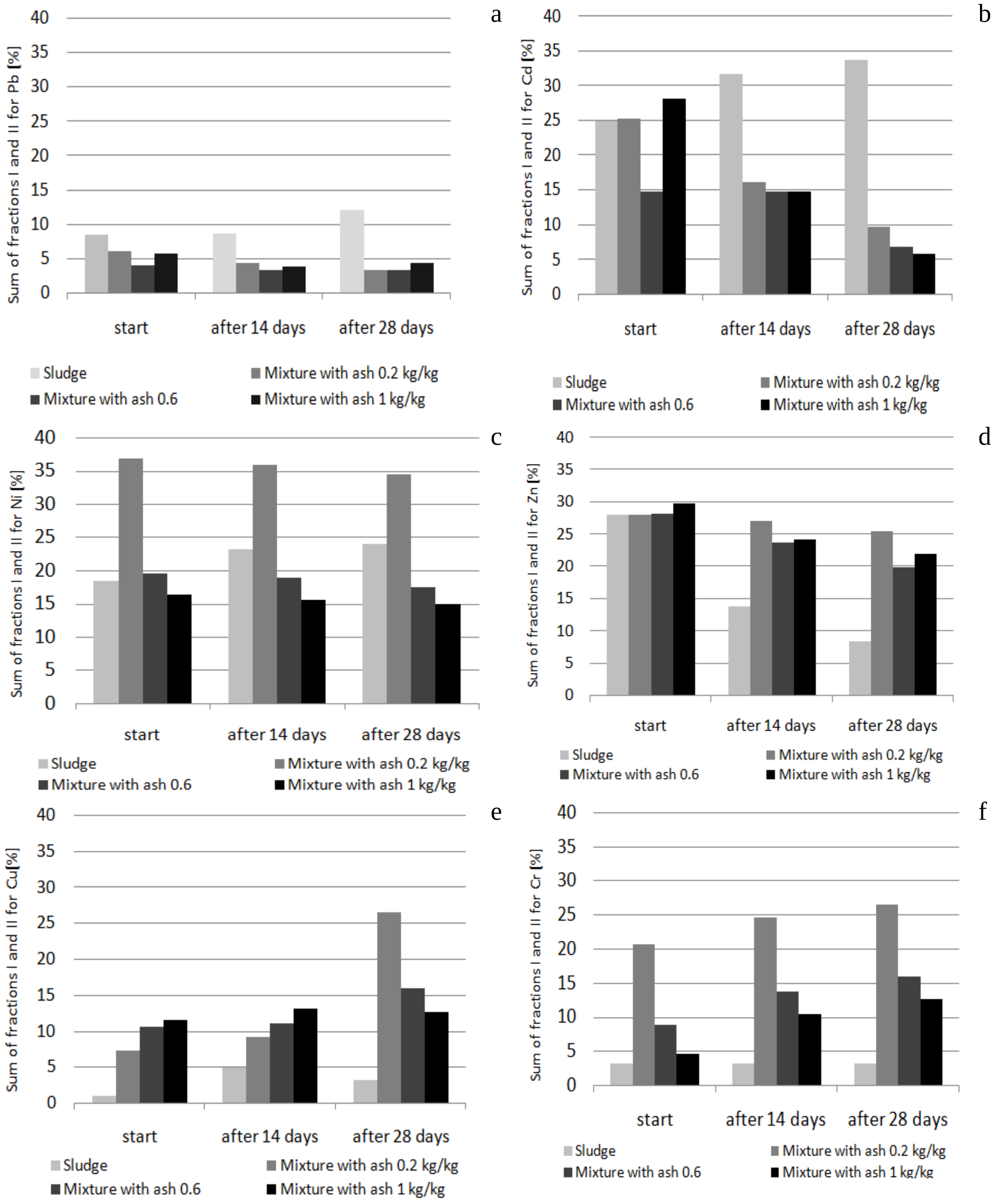

Fig. 4. Time dependent changes in share of mobile fractions (sum of I and II fraction) of:
(a) lead, (b) cadmium in the sludge and sludge-ash mixtures;
(c) nickel, (d) zinc, (e) copper and (f) chromium in the sludge and sludge-ash mixtures

Changes in lead fractions percentage

The lead was bound in sewage sludge in following order of fractions: V > IV > III > II > I (Fig. 2a). The addition of high doses of ashes changed the order of the fractions. In the case of dose 0.6kg/kg d.m. the share of fractions IV and III became equal, while in the case of the highest dose of ash, the share of fraction III exceeded fraction IV (Fig. 2a). The sums of two main fractions exceed 72% of total amount of lead.

The highest dose of fly ash resulted in a slight decrease of fraction I, II, and IV in favor of fraction V. Lead was bound in sewage sludge mainly in fraction V (the residue-bound fraction) which is in line with the observations of *Zufiaurre et al.* [21], and an addition of ash increased the value of this parameter (Fig. 2a). Generally, the share of Pb in fraction V in all the sludge-ash mixtures was growing with the time of the experiment (Tables 4-6). While increasing the dose of fly ash, the concentration of lead in fraction V showed the tendency to increase. In the case of maximum dose of ash, Pb content in fraction V increased 1.13-times (up to 49.28%) immediately the addition, and over 1.5 times (up to 68.18%) after 28 days of the experiment (Tables 4-6).

Fraction IV – the fraction bound to organic matter – forms the second largest fraction and constitutes approximately 30% (Fig. 2a), of the total amount of lead contained in the sewage sludge. The share of this fraction was decreased to the value of 20.6% immediately after the highest dose of fly ash was added, and up to value of 7.6% after 28 days of the experiment (Fig. 3a).

In the case of fraction III, an increase in its share by 5.58% was observed (from 18.82% to 24.40%) (Fig. 3a).

After 28 days of the experiment, lead was bound in the sewage sludge alone in the following order of fractions: V>IV>III>I>II (Fig. 3a). Slight increases in the shares of fraction I and III were noted. In the case of fraction I, it increased by 2.49% (from 3.15% to 7.85%). However, the share of lead in this fraction decreased along with the fly ash dose (0.2 and 0.6kg fly ash/kg d.m.) (Table 6), whereas it slightly increased to 1.95% at the dose of 1.0kg fly ash/kg d.m. (Fig. 3a). In the case of fraction III, its share also increased by 5.49% (from 18.82% to 24.31%) (Fig. 3a). Fly ash addition resulted in further increases in the least available fractions IV and V, reaching 75.78% of total lead amount.

The sum of fractions I and II (Fig. 4a), which represents the bioavailability of the metals [22] showed that Pb is low bioavailable in all the examined materials.

Changes in cadmium fractions percentage

Cadmium in the sewage sludge was bound in the following order of fractions: V>III>IV>II>I (Fig. 2b). In the bioavailable fractions I and II, it has the total share of 24.85% (Fig. 4b). Fly ash addition resulted in slightly increased shares of cadmium in these fractions (Fig. 2b). In the case of fraction I, from the initial value of 12.25% in sewage sludge alone, it increased to 14.20%, while in fraction II – from 12.60% to 13.90% (Fig. 2b). As far as fraction I is concerned, this property can be attributed to the fact that the cadmium in fly ash occurs in the form adsorbed on the surface of ash particles; thus, it is relatively easily released [23].

The fly ash addition to sludges caused changes mainly in fractions III and V. In the former, a marked decrease by 7.48% occurred after the addition of lowest fly ash dose – from 27.10% to 19.02% (Fig. 2b). Slight mobilization of cadmium was probably induced by its removal from the sorption complex by alkaline metal cations Ca^{2+} and Mg^{2+}, which was supplied with the ash [24].

Increase in the pH of the system with the increase of dose of ash resulted in slight fluctuations in the share of this metal in fraction III. In the case of fraction V, a clear increase in its share was noted at the maximum fly ash dose of 1.0kg fly ash/kg d.m. – from 30.70% to 38.67% (Fig. 2b).

A relatively high cadmium level, i.e. 17.35%, was also observed in fraction IV bound with organic matter, which protects microorganisms against the toxic effect of this metal. The share in fraction IV gradually decreased with increasing fly ash addition (to 14.21%) in favor of fractions III and V (Fig. 2b).

After 28 days of solidification in sewage sludge, cadmium slightly increased its shares in fraction I, reaching the maximum value of 17.05% (Fig. 3b). In the case of the highest fly ash dose in sludge-fly ash mixtures, the shares in fraction I decreased from 14.20% do 3.20% (Fig. 3b). Content of fraction II (bound to carbonates) increased by 4.07% for the sewage sludge without fly ash addition (Fig. 3b). In turn, a clear decrease occurred in fraction II when fly ash was applied. It decreased from 12.72% to 4.95% for the mixture with dose of 0.2kg fly ash/kg d.m (Tables 4-6) and from 13.90% to 2.53% for 1.0kg fly ash/kg d.m. (Fig. 3b).

In fraction III, the greatest decreases in cadmium shares, reaching 15.42% (from 27.10 to 11.42%) occurred in sewage sludge alone. In the case of sludge-fly ash mixtures, these decreases were smaller and amounted to 1.12% for 0.2kg fly ash/kg d.m (from 19.62% to 18.50% – Tables 4-6) as well as 0.86% for the maximum dose of 1.0kg fly ash/kg d.m (from 18.02 to 18.16% – Fig. 3b).

Fraction IV also decreased its shares after 28 days of the experiment. In the case of sewage sludge alone, its content dropped by 10.05% (from 17.35% to 7.30%), whereas with fly ash addition: by 10.25% (from 17.15% to 6.90%) for 0.2kg fly ash/kg d.m, by 10.51% (from 16.21% to 5.7%) for 0.6kg fly ash/kg d.m, and by 9.09% (from 14.21% to 5.12%) for 1.0kg fly ash/kg d.m (Tables 4-6).

Fraction V, which is characterized by the lowest bioavailability, increased its shares significantly within time, both in sewage sludge alone – by 16.56% (from 30.70% to 47.56%) – and with fly ash addition. In the case of 0.2kg fly ash/kg d.m, it increased by 26.95% (from 38.02% to 64.95%), for ash dose of 0.6kg/kg d.m it was raised by 31.52% (from 38.62% to 70.52%), whereas for ash dose of 1.0kg/kg d.m it increased by 32.32% (from 38.67% to 70.99) (Tables 4-6). This indicates a significant influence of ash addition on forming stable polymineral complexes of cadmium with aluminosilicates [25].

Changes in nickel fraction percentage

Nickel was bounded sewage sludge in the following order of fractions: III<IV<V<I<II (Fig. 2c). In the bioavailable fractions I and II in sewage sludge, nickel has the total share of 18.35% (Fig. 4c). The fly ash addition changed the order of fractions. At the lowest dose of 0.2kg fly ash/kg d.m, a relatively large change in the concentrations of this metal in particular fractions was noted. Significant increases in bonding with fraction I, II, and V were observed, by and over 1.3-fold (up to 12.35%), 2.6-fold (up to 24.55%) and 1.7-fold (up to 32.44%), respectively (Fig. 2c). A significant decrease in nickel bounded in fraction III, was observed in all the mixtures compared to the sewage sludge (Tables 4 and 6), where it formed more organic complexes [24].

Along with fly ash addition, an increase in nickel concentration in fraction V and systematic decreases in the remaining fractions were observed (Fig. 2c). The shares in fraction IV changed the fastest; from 26.20% prior to the fly ash addition, to 17.45%, 16.21%, and 15.20%, depending on the fly ash dose. At the highest dose of fly ash, the order of fractions was as follows V<III<IV<I<II (Fig. 2c). At the dose of 1.0kg fly ash /kg d.m, slight changes were observed in fraction I and II, there was also a drop in percent share in fraction III (by 13.77%) and IV (by 11.0%). Over 2.4-fold increase in nickel concentration (up to 45.74%) was observed only in fraction V (Fig. 2c).

After 28 days of stabilization in sewage sludge alone, nickel was bound with particular fractions in the following order: V<III<IV<<I<II (Fig.3 c). The differences are related to a 6.4% increase in share of fraction V (from 18.95% to 25.35%) and increased in the most mobile fractions I and II, in total by over 5.6%, as well as decrease in fractions III and IV by 5.31% and 6.75%, respectively, compared to the sewage sludge alone (Fig. 3c).

In the case of sewage sludge with the highest addition of fly ash, after 28 days of stabilization, nickel was bound with the following fractions: V<III<I<VI<II (Fig. 3c). The total concentration of Ni in the least bioavailable fractions (IV and V) was 63.63%.

Fraction III, bound with carbonates, in the case of sewage sludge alone, constituted 36.50% of total nickel content. Following the fly ash addition, its share decreased, reaching 22.73% at maximum dose. After 28 days of stabilization, the share of nickel further decreased slightly to 21.45% (Fig. 3c).

The share of nickel in fraction V in sewage sludge amounted to 18.95%. During the experiment, the maximum fly ash dose increased the level of nickel to 45.74%, while after 28 days – to 58.91% (Fig. 3c). Taking into account the significant immobilization of this element, it should be stated that even at high concentrations of this metal, the sewage sludge treated with fly ash should not pose a threat for the environment. But, on the other hand, an increase in the acidity of the soil environment may be able to be a reason of increase in mobility and bioavailability of nickel [26].

The growing immobilization of nickel after ash addition, expressed in the decrease of total share of the most mobile fractions (I and II) (Fig. 4c) can be explained by increasing pH values of the mixtures (Fig. 5).

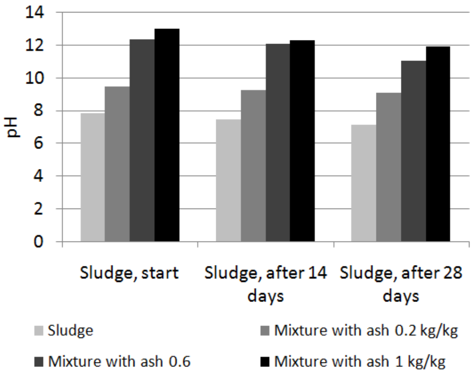

Fig. 5. An influence of fly ash addition on pH values of the examined materials observed within the experiment

Changes in zinc fraction percentage

Zinc was bound with sewage sludge in the following order of fractions: III<II<V<IV<I (Fig. 2d). In bioavailable fractions I and II, zinc has 28% of total share in sewage sludge (Fig. 4d). The highest concentrations of this element were observed in fraction III, which constitutes over 50% of total zinc concentration in sewage sludge (Fig. 2d). This fraction is vulnerable to the changes in redox potential [21]. The high share of zinc in fraction III (bound with iron and manganese oxides) in the examined sewage sludge can be attributed to a use of iron added in the form of PIX in order to precipitate hardly soluble iron phosphates during the wastewater treatment [24, 27].

Along with fly ash addition and its increasing doses, the share of zinc in fraction III connected with iron and manganese oxides was further raised to 54.10% at maximum dose of fly ash (Fig. 2d). The share of zinc in fraction IV decreased with increasing fly ash addition. At the beginning of the experiment the share of this metal in sewage sludge amounted to 7.90%, and it was gradually reduced with an increase of fly ash dose, to value 4.35% (in the mixture with 1.0 kg ash/kg d.m of sludge). In time, this share was further reduced and at the maximum dose of fly ash, it dropped to 2.50% after 14 days and to 1.89% after 28 days (Fig. 3d).

Fraction V is characterized by the lowest bioavailability and its share reached 12.88%. During the experiment, the percent share increased to 48.75% after 14 days and maintained an increasing trend, reaching 61.77% after 28 days of the experiment (Fig. 3d).

The fly ash addition reduced the share of zinc in fraction V, which was slightly decreased to 11.35% at the maximum dose of 1.0kg fly ash/kg d.m (Fig. 3d). However, it should be noted that in each dose, starting from 0.2kg fly ash/kg d.m, the initial share of zinc equal to 14.28% increased by over 8% (to 22.37%) in the 28th day of the experiment. This trend was maintained for other doses: for the dose of 0.6kg fly ash/kg d.m, it increased by over 7.6%

(to 26.13%). At the maximum dose, the initial zinc concentration was 11.35% and after 28 days of the experiment, its concentration in fraction V increased by over 11%, to 22.59% (Table 6).

Fraction V is characterized by the lowest bioavailability and its share in sewage sludge reached 12.88%. During the experiment, the percent share of this fraction increased to 48.75% after 14 days, and to 61.77% after 28 days of the experiment (Fig. 3d). The fly ash addition reduced the share of zinc in fraction V. The share of this fraction in the mixture with maximum dose of 1.0kg fly ash/kg d.m. was only 11.35% (Fig. 3d). However, it should be noted that in each dose of ash, the initial share of zinc in fraction V increased within time of the experiment (Tables 4-6). At the maximum ash dose, the initial zinc share in fraction V was 11.35% and after 28 days of the experiment, its value increased by over 11%, to 22.59% (Table 6).

According to the data presented in Fig 4d it can be stated that this element is difficult to immobilize. It can be caused by the competition of Zn^{2+} and Ca^{2+} for the available active centers, because these ions have similar ionic radii. The high mobility of nickel is consistent with the results of the study by Sackar et al. [28].

Fly ash addition to the sludge resulted in slight (by 1.65%) increase in share of this metal in fractions I and II. At the maximum dose of ash the sum of these fractions amounted to 29.65% (Fig. 4d). Taking into account particular doses of fly ash, decreases in particular shares of zinc in fractions I and II were noted as a function of experiment time. For the dose of 0.2kg fly ash/kg d.m., reduction reached 2.51% (from 27.93% to 25.42%), for 0.6kg fly ash/kg d.m – 8.25% (from 28.15% to 19.90%), while for the maximum dose of 1.0kg fly ash/kg d.m – 7.71% (from 29.65% to 21.94%). Longer contact time probably enhance incorporation of zinc into crystallite structures formed in sludge-fly ash mixtures (tables 4 and 6).

Changes in copper fraction percentage

Copper was bound in sewage sludge in the following order of fractions: IV<V<I<III<II (Fig. 2e). The bioavailable fractions (sum of fraction I and II) are estimated on 1% (Fig. 4e). The share of fraction III was also very low (0.50%), but the most of cooper was bound in fraction IV (88.21%) (Fig. 2e). The highest share of cooper in fraction IV in sewage sludge was also observed by Zufiaurre [26]. Fraction V had a slightly higher share of 10.29% (Fig. 2e). However, the highest share of this element was found in fraction IV. This fraction is vulnerable to any changes in pH and redox potential of sludge water.

The fly ash addition reduced the content of copper in fraction IV, at maximum dose the share of fly ash dropped by 26.76% and reached 61.45% (Fig. 2e). The concentration of Cu in the fraction bound with organic matter decreased with time, thus increasing the share in fraction V. After 28 days of the experiment, the copper in sewage sludge was bound with fractions in the following order V<IV<I<II<III (Fig. 3e). Substantial increase in shares occurred in four fractions: in fraction I – by over 8-fold, II – over 4.7-fold, III – over 1.6-fold, and V – over 4.7-fold (Fig. 3e).

In sewage sludge in a strongly alkaline environment, the increase in ion-exchange forms of copper can be explained by the formation of mobile anionic forms $[Cu(OH)_3]^-$, $[Cu(OH)_4]^{2-}$ and $[Cu(CO_3)_2]^{2-}$ [27, 29] .

In turn, the share in fraction IV was almost halved (Fig. 3e). Very high organic fraction share after long time indicates that a major part of this metal may occur in the stable form of porphyrin complexes or be bound with other organic ligands which are stable and resistant to pH. The bonding of Cu with fraction V, with equally high share of fraction IV, increased along with the solidification time and fly ash dose. Combined, fractions IV and V, accounted for 84.51% (Fig. 3e).

The bioavailability of copper largely depends on environmental factors, such as pH, redox potential (Eh), type of soil and sludge, hardness of water, and the content of organic substances. These factors vary in the environment, contributing to the possible Cu deficiency conditions or its toxicity.

Figure 6a and b present exemplary graphs showing the dependence between the share of selected fractions of copper and TOC value measure in sewage sludge and particular mixtures.

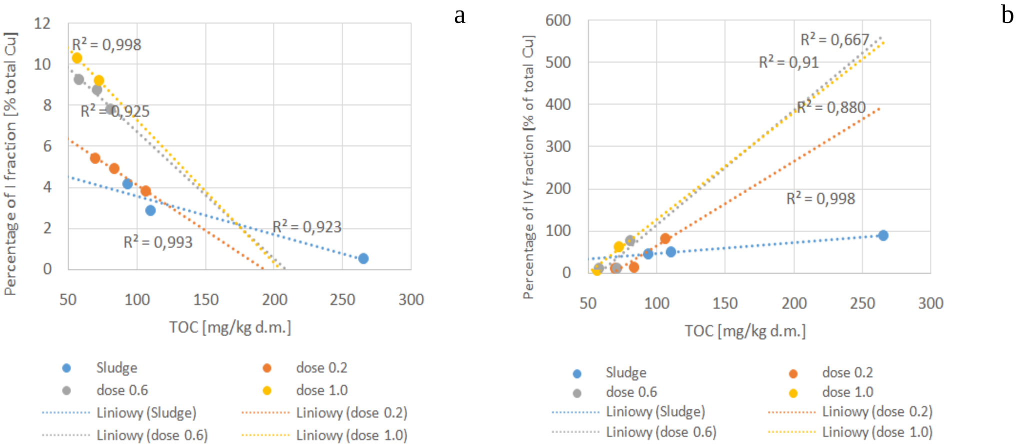

Fig. 6. Dependence between TOC and copper concentration in fraction I (a) and IV (b)

This indicate that in the case of copper, an increase in TOC is strictly connected with the Cu content decrease in fraction I for sewage sludge as well as all mixtures of sludge and fly ash. In contrast, an increase in TOC is strictly positively correlated with an increase in the share of copper in fraction IV.

Changes in chromium fraction percentage

Chromium in the sludge was bound with the fractions in the following order: IV>III>V>I and II (Fig. 2f). In the bioavailable fractions I and II, the total share of chromium in sewage sludge amounted to 3.20% (Fig. 4f).The main factors affecting the form and sorption of chromium are redox potential and pH [24]. The fly ash addition at the lowest dose of 0.2kg/kg d.m. increased the share in fractions I and II, i.e. exchangeable and bound with carbonates, respectively. The share in fraction I increased by 6.8-fold, in relation to the sewage sludge alone, and reached 10.92% (Fig. 2f). Similarly, fraction II increased by over 6-fold (to 9.76%), whereas fraction III increased by approximately 1.5-fold (to 34.02%) (Fig. 2f). The fly ash addition to sewage sludge caused a small increase in the share of chrome in labile fractions I and II, which resulted from the presence of Cr^{3+} ions adsorbed on fly ash particles. However, this increase should not reduce the toxicological safety of the sludge-fly ash mixtures (the chromium concentration in labile fractions was well below the permissible values). In turn, the fraction of fraction IV – bound with organic matter – was reduced by almost 1.6-fold (to 34.02%), while fraction V – by 3-fold (to 6.90%).

Increasing the fly ash dose reduced the most bioavailable fractions I, II, as well as increased the shares in fraction V to 41.85% (Fig. 2f). Initially, the shares of fraction I and II increased and then they slowly decreased (Fig. 2f). In the case of fraction III, it should be noted that in the mixtures the shares in this fraction are higher than in the sewage sludge alone. The shares of fraction IV decreased with the fly ash dose, reaching 26.45% at the maximum dose. Fraction V was the only one which increased its share with the dose of ash. But, compared to sewage sludge the share of this fraction decreased from 20.80% to 6.90% (Fig. 2f).

Taking into account the experiment time, after 14 and 28 days, at the dose of 1.0kg fly ash/kg d.m, the order of fractions was as follows: V>IV>III>II>I (Fig. 4f). At maximum dose, the highest shares, reaching 67.28%, were obtained in fraction V (Fig. 3f). From the very beginning of the experiment, fraction V increased its shares both as a function of time as well as fly ash dose (Table 4-6). This may indicate that chromium is incorporated into the structure of aluminosilicate crystallites, as well as the structures similar to zeolites, in which the Al^{3+} ions were partially substituted with Cr^{3+}. This is confirmed by the decreasing share of fraction IV (initially amounting to 53.10%), which reduces along with fly ash dose as well as experiment time. The fact that mineralization of this fraction was initially fast and then slowed down may indicate the occurrence of numerous organic complexes of chromium in sewage sludge, characterized by varying stability.

In sewage sludge alone, chromium reduced its share in fraction III, after 28 days of the experiment by over 3%, whereas at maximum fly ash dose – by over 14% (Fig. 3f). The share of chromium in fraction II exhibited over 4-fold increase (from 1.60% for sewage sludge to 6.50% at maximum fly ash dose – Table 4 and 6).

At the maximum dose of ash, fraction I, which is characterized by the greatest bioavailability, increased its shares by over 3.8-fold after 28 days of the experiment (Fig. 3f). The sum of the fraction I and II was also increased with time in all the mixtures (Fig. 4f).

Conclusions

The reuse of waste has currently become a global trend in waste disposal. The natural utilization of waste is one of the directions for the waste management. However, the minimization of its negative impact on the environment is the major requirement to be met. Knowledge of the total content of heavy metals in sewage sludge and fly ash does not reflect their potential threat to ecosystems. Their availability in the environment depends on mobility, which in turn is related with their form of occurrence.

The results of the sequential analysis indicated that:

- All of the analyzed metals in the sewage sludge alone increase their share in fraction V with the passing time of the experiment. The lowest dose of fly ash from lignite combustion caused a marked increase in the fraction characterized by lowest availability in the case of: lead, cadmium, nickel and zinc; in turn, but its addition caused a decrease in the shares in fraction V of two metals: copper and chromium.
- Only a dose of 0.6kg fly ash/kg d.m caused a significant increase in the share of all analyzed metals in this fraction.
- In the case of fraction I – characterized by the greatest bioavailability – for the sewage sludge alone, the time dependent increase in share of this fraction was noted for the following metals: lead, cadmium, nickel and copper, while in case of zinc and chromium the decrease of this parameter was observed. The fly ash addition caused a decrease in the shares in fraction I of the following metals: lead, zinc, and increase for copper and chromium. In the case of nickel, depending on the dose, an initial increase was observed with the addition of 0.2kg fly ash/kg d.m followed by a decrease in the share of this metal. This regularity was also maintained with the passing experiment time. - Low concentrations of heavy metals in sewage sludge and sludge-ash mixtures indicate no risk of contamination of the environment with heavy metals as a result of introducing such mixtures into the soil.

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Received: April 19, 2021
Accepted: July 20, 2021