Original Research

The Mobility of Chosen Pollutants from Ash-Sludge Mixtures

Cz. Rosik-Dulewska[1*], K. Głowala[1], U. Karwaczyńska[2], E. Szydło[2]

[1]Department of Earth Surface Protection, Institute of Environmental Engineering of the Polish Academy of Sciences, 34 M. Curie-Skłodowskiej St., 41-819 Zabrze, Poland
[2]Department of Natural Sciences and Technology, Faculty of Earth Surface Protection, Opole University, 22 Oleska St., 45-952 Opole, Poland

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Abstract

Both sewage sludge and fly ash are wastes. Their granulation can decrease their adverse effect. Due to the contents of biogens in the sewage sludge the granulates will have fertilizing and soil-forming properties. The aim of this study was to find such proportion of components used for production of ash-sludge granulates that would decrease the volume of extracted contaminants to meet the requirements of regulation [36] preserving their fertilizing properties. In our study two types of fly ash were mixed in various proportions with municipal stabilized sewage sludge. The obtained granulates were subjected to one- and three-stage elution tests. In the eluates the concentration of nitrogen compounds, phosphorus, magnesium, calcium and heavy metals was determined. The mixture with the same share of sewage sludge and fly ash proved to be of high fertilizing value at the same time.

Keywords: sewage sludge, fly-ash, granulation, elution test

Introduction

Water supply is accompanied by the necessity of solving the problem of collecting and treating increasing volumes of wastewater and, in consequence, handling and utilization of the sewage sludge generated in these processes. At present, a significant volume of sewage sludge is disposed on-site at the wastewater treatment plants or at municipal landfills.

Limited capacity of the municipal landfill sites and more stringent requirements related to environmental protection stimulate an intensive search for sewage sludge utilization methods other than disposal. Special stress has been put on these methods which allow for multiple sludge applications, after elimination of its sanitary risks, accompanied by a positive economic effect.

*Corresponding author; e-mail: dulewska@ipis.zabrze.pl

Sewage sludge may be used for industrial and non-industrial (natural) purposes. Industrial applications include thermal processing methods consisting in sludge combustion with or without other combustible additives and energy recovery [1-5], and the application of pyrolisis or gasification leading to production of flammable gases as well as liquid and solid pyrolysis products which are then used as fuels [1, 6-9]. Studies are also ongoing on sewage sludge ash application for production of different materials, e.g. granulate for hydraulic feelings in underground mines, as a component of construction materials, etc. [10-14].

The soil-formation and fertilizing qualities of sewage sludge resulting from the high content of organic matter, nitrogen, phosphorus, magnesium, calcium and microelements make natural sludge application one of its most effective solutions, under the assumption that all the requirements for sludge used for non-industrial purposes are met. Conditions that must be fulfilled at natural sludge application are subject to the Regulation of the Minister of Environmental Protection, Natural Resources and Forestry of 1 August 2002 (Journal of Laws No.134, item 1140) [15].

This Regulation transposes rules operating in the EU (Directive 86/278/EEC [16]), and what is more according to Polish Law the maximum permissible content of the majority standardized heavy metals is lower than that given in the Directive.

Municipal sewage sludge and sludge composts made with the addition of other organic waste materials (e.g. wood chips, bark, plant waste), organic fraction of municipal waste or other additives may be used for reclamation purposes of degraded areas or idle land, organic fertilization of arable land and forest land (nurseries, wood production), urban areas (e.g.: urban green areas), industrial sites, drainage soil fertilization and plant production for composting [17-27].

A number of sewage sludge application methods are used at present, one of which is a direct application of liquid or soil-like digested sludge at the site. The key problem of sludge application for natural purposes is its greasy consistency, making transport and odour problem.

Other groups of waste of equal noxiousness to the environment is fine-grained ash (fly ash) from energy production. Hazardous substances contained in it include heavy metals, sulphur compounds, etc., together with the fine-grain size that constitute risks during its disposal.

Binding properties of fly ash may be successfully implemented for solidification of different materials including sewage sludge in the form of blocks, briquettes and granules [22]. Fly ash also is an ideal component for sludge hygienization and stabilization due to its chemical composition, fine-grain form and alkalising properties. Fly-ash eliminates the hazard of pathogens contained in sludge as well as unpleasant odour emission [25, 28-30].

Numerous studies have proven that solidification of fly ash and sewage sludge allows for production of mineral and organic composites, e.g. fly ash – sludge mixtures of fertilising properties. They show considerably better physical and chemical properties that enable their transport and disposal compared to the waste material they originate from [30]. Moreover, these mixtures contain a significant amount of organic matter and as such may be successfully utilized for land improvement and reclamation of arable as well as degraded soils using conventional agricultural equipment for fertilizer or manure application [19, 29, 32, 33].

The technology of sewage sludge and fly ash processing to mineral and organic composites is related to the application of a special technological installation with plate or drum granulators enabling mixing and application of different fly ash types and doses. There is no dust emission from granulates during transportation and disposal, they are characterized by a round shape of grains, mechanical resistance, equal distribution of grain composition and good cohesion [34].

Natural use of the ash-sludge composites presented in this paper will be possible when their fertilizing properties will be accompanied by non-hazardous effect on quality of underground water, ground water and soil. Thus, it seems to be of importance to know not only concentration of individual components in the granulate dry matter but

Table 1. Properties of fly-ash.

No.	Determined index	Symbol	Unit	Determination value	
				Bełchatów	Łaziska
1.	Fly-ash content	A^a	%	98.2	96.1
2.	Weigh loss on heating	–	%	1.8	3.9
3.	Silicon oxide (IV)	SiO_2	%	50.36	50.14
4.	Aluminium oxide	Al_2O_3	%	22.92	26.96
5.	Calcium oxide	CaO	%	12.88	3.71
6.	Iron oxide(III)	Fe_2O_3	%	4.48	5.58
7.	Sulphur oxide(VI)	SO_3	%	4.03	0.63
8.	Magnesium oxide	MgO	%	1.52	1.97
9.	Titan oxide(IV)	TiO_2	%	1.16	1.06
10.	Phosphorus oxide(V)	P_4O_{10} (P_2O_5)	%	0.26	0.67
11.	Potassium oxide	K_2O	%	0.21	3.06
12.	Sodium oxide	Na_2O	%	0.11	0.78
13.	Manganese oxide(II and III)	Mn_3O_4 ($MnO{\cdot}Mn_2O_3$)	%	0.03	0.06

also the rate and quantity of components released from the granulate to the environment. It is advisible that indices eluated from the granulates, recognized as contamitants, will not exceed the permissible level for sewage disposed into water and soil (*Regulation of the Minister of Environment on the conditions that must be fulfilled at final effluent discharge to the waters or soil and on substances especially hazardous to the water environment* [35]).

The aim of the study was to fit such proportion of components used for the ash-sludge granulates forming to ensure optimal effect of the final product on the ecosystem, i.e. the volume of the potential contamitants released from the granulates into the soil-water environment should not exceed the permissible level for sewage disposed to water and soil and at the same time the rate of biogen release should be time-distributed to ensure their successive uptake by plants.

This paper deals only with the mobility of contaminate indices eluated and biogens from the ash-sludge components.

Characteristics of the Investigated Material

As material used for the experimental studies, mixed fly ash-sludge granulates were used. The granulates were made of a mixture of fly ash from lignite combustion at the Bałchatów Power Plant and hard coal combustion at the Łaziska Power Plant (Table 1) and sewage sludge from the Zabrze-Śródmieście Municipal Wastewater Treatment Plant (Table 2). No binding agents or binding activators were added for granulate production. The quantitative ratio of sludge and fly-ash content in mixtures used for granulate production was 3:7 (N9), 1:1 (N10) and 7:3 (N14). Fly ash from the Bełchatów Power Plant was used in the first two granulates: N 9 and N 10, and from Łaziska Power Plant in granulate N 14. Granulate N 9, of dark grey colour and dominant fly-ash content, is characterized by a low mechanical resistance and diversified grain size. Granulate N 10, of equal sludge to fly-ash weight ratio, is black, and is characterized by a rather low mechanical resistance while the grain diameter is smaller and more homogenous compared to granulate N 9. Granulate N 14 of black colour and dominant sludge content is characterised by high hardness and fine grain size.

Experimental Procedure

In the study two protocols of water extract preparation were used:

– According to the Regulation of the Council of Ministers of 21 December 1999 amending the regulation on waste disposal tariffs (Journal of Laws Dz.U. of 1999, No 110, item 1263 – presently suspended) [36],
– According to the Polish Norm PN-Z-15009. Solid wastes. Preparation of water extract [37].

According to the above-note regulation a single-stage extraction was carried out. Granulate samples were poured with distilled water (the 1 part of dry matter to 10 parts of water ratio) and then were shaken for 4 h and left for sedimentation. The samples were shaken for 2 h and left for sedimentation again. Total extraction time amounted to 18 h, and the extraction was carried out at a room temperature.

Three-stage extraction was carried out according to the above-mentioned standard. The granulate samples were poured with distilled water (the 1 part of dry matter to 10 parts of water ratio) and left for 1 h. Each of 3 extraction stages was carried out as follows: samples were shaken for 4 h and then left for sedimentation, samples were shaken again and left for sedimentation each time with a new portion of water. Total extraction time amounted to 78 h. The extraction was carried out at room temperature with a control of extracts reaction from successive elution stages.

The obtained extracts in the one and three-stage tests of elution were filtered through a filter paper and ana-

Table 2. Properties of sewage sludge from the Zabrze-Śródmieście Wastewater Treatment Plant.

No.	Determined index	Unit	Determination value
1.	Dry mass content	% weight.	14.00
2.	Water content	% weight.	86.00
3.	Mineral substance content	% d.m.	58.13
4.	Organic substance content	% d.m.	41.87
5.	Heavy metal content: Cu Zn Cd Ni Pb Cr Hg	mg kg^{-1} d.m.	 155.68 3569.35 3.09 20.74 187.07 36.89 1.99

lyzed according to Polish Standards in force. Basic physical indices were determined and chemical analyses were carried out to determine the concentration of biogens and metals, including heavy metals. Index analysis was made using PHILIPS PU 8620 spectrophotometer while heavy metals, were determined using atomic absorption spectrometry (AAS) on a UNICAM-PHILIPS PU 9100 X spectrometer.

Loads of eluted contaminants were calculated according to the following formula:

$$A=(C \times L)/M_D$$

A – load of eluted contaminant [mg kg^{-1}]
C – concentration of individual component in extract [mg l^{-1}]
L – water volume used [l]
M_D – weight of the granulate dry matter [kg]

Results and Discussion

Composition of eluates obtained in tests of elution depends not only on chemical composition of ash and sewage sludge but also on processes occurring in results of both materials fusion in the granulate form. One- and three-stage tests of ash-sludge mixtures N 9, N 10 and N 14 elution were performed to determine potential hazard of granulates for the environment.

The water extracts of this test were characterized by (Table 3):

- alkaline reaction, with a slight pH increase corresponding to the increase of sludge content in the mixture (from 8.21 (N9), 8.25 (N 10) to 8.34 (N 14)). The slight difference in pH of water extracts of the analyzed granulates is due to the higher pH of ash water extract from hard coal (Łaziska – N14) when compared to the ash water extract from lignite (Bełchatów– N9 and N10),which in turn results from different content of calcium, potassium and sodium oxides in ashes. For example, the percentage content of K_2O and Na_2O (Łaziska – N14) is 7 and 11 times higher, respectively, in ash from hard coal,
- colour, falling in the range of 100-200 mg l^{-1} Pt, increasing correspondingly to an increase of the sludge content in the granulate i.e. N 9<N 10<N 14,
- high electrical conductivity (the lowest for N9 extract – 2610 µS cm^{-1}, the highest for N 14 extract – 3230 µS cm^{-1}). Similarly, as in the case of the colour, the con-

Table 3. Results of the chemical analyses of water extracts from fly ash-sludge granulates N 9, N 10, N 14 (single-stage elution test).

No.	Determined index	Unit	Determination value		
			N 9	N 10	**N 14**
1.	Reaction	–	8.21	8.25	8.34
2.	Colour	mg l^{-1}Pt	100	160	200
3.	Odour	–	ZG4	ZG4	ZG4
4.	Electrical conductivity	µS cm^{-1}	2610	3170	3230
5.	Ammonia nitrogen	mg l^{-1}	**88.82**	**150.62**	**231.35**
6.	Nitrite nitrogen	mg l^{-1}	0.017	0.027	0.023
7.	Nitrate nitrogen	mg l^{-1}	0.478	0.94	1.43
8.	o-phosphates	mg l^{-1}	2.5	7.3	16.7
9.	Sulfates	mg l^{-1}	**938.2**	**1082.2**	**950.6**
10.	Chlorides	mg l^{-1}	139	145	124
11.	Calcium	mg l^{-1}	396.9	323.4	411.6
12.	Magnesium	mg l^{-1}	164.3	11.9	85.7
13.	Iron	mg l^{-1}	4.25	1.70	1.40
14.	COD $_{KMnO_4}$	mg l$^{-1}O_2$	137.6	215.6	220.6
15.	COD $_{K_2Cr_2O_4}$	mg l$^{-1}O_2$	**650**	**1380**	**1300**
16.	Cu Zn Cd Ni Pb Cr	mg l^{-1}	0.18 0.66 0.13 0.06 <0.01 0.04	0.16 1.06 0.15 0.06 <0.01 <0.04	0.16 1.53 0.14 0.09 <0.01 0.04

ductivity increased alongside with the increase of the sludge content in the mixture i.e.: N 9<N 10<N 14.

Based on the analysis of the water extracts of N 9, N 10 and N 14 granulates (Table 3), the loads of the eluted nutrient and contaminant indices were calculated in mg kg^{-1} d.m. (Table 5).

The analyzed granulates were characterized by:

– high load of the eluted ammonia nitrogen (888-2314 mg kg^{-1} d.m.) at low load of the eluted nitrogen, both: nitrite (0.17-0.23 mg kg^{-1} d.m.) and nitrate (4.78-14.3 mg kg^{-1} d.m.). Concentration of the ammonia nitrogen in the water extract from the mixtures: N 9, N 10 and N 14 exceeded the permissible value for effluent discharged to waters and soils (10 mg N_{NH4} l^{-1}) [1] (Table 3),
– o-phosphates in the range of 25-167 mg kg^{-1} d.m.,
– a very high load of the eluted sulphates (in the range of 9382-10822 mg kg^{-1} d.m.). Sulphate content in the water extract (Table 3) exceeded the permissible value for effluent discharged to waters and soils (500 mg l^{-1}) by two times,
– high content of organic compounds determined as dichromate COD, in the range of 6500-13800 mg kg^{-1} d.m., whereas the permissible value of this index for municipal sewage is 125-150 mgO_2 l^{-1} and for industrial is 125-250 mgO_2 l^{-1}.

For such indices as ammonia nitrogen, o-phosphates, sulphates, COD $KMnO_4$, COD $K_2Cr_2O_7$ as well as zinc, an increase of the elution level was observed at increasing sludge content in the mixture, i.e.: N 9<N 10<N 14 (Table 5). On the contrary, in the case of iron, its highest load was eluted from the N 9 mixture (42.5 mg kg^{-1} d.m.) and the lowest from the N 14 mixture (14.0 mg kg^{-1} d.m.). It proved that the eluted iron load decreased at a decrease in the fly ash content in the investigated mixtures i.e.: N 9>N 10>N 14 (Table 5).

For the other indices i.e.: chlorides, calcium, magnesium, copper, cadmium, nickel, lead and chromium, no correlation was identified between the composition of the fly-ash sludge mixtures: N 9, N 10, N 14 (i.e. the sewage sludge and fly ash ratio) and the indices' elution load.

The other conducted elution test comprised three elution stages of the investigated material. The water extracts from the three-stage test were characterized by the following parameters (Table 4):

– reaction in the range of 7.13-7.53, depending on the type of mixture and elution level. An increase of pH alongside with an increase of the elution level was

Table 4. Results of the chemical analyses of water extracts from fly ash-sludge granulates N 9, N 10, N 14 (three-stage elution test).

No.	Determined index	Unit	Determination value								
			N 9			N 10			N 14		
			1°	2°	3°	1°	2°	3°	1°	2°	3°
1.	Reaction	–	7.53	7.47	7.50	7.13	7.17	7.26	7.20	7.14	7.22
2.	Colour	mg l^{-1}Pt	60	60	40	150	100	60	250	140	140
3.	Odour	–	ZG3	ZG3	ZG2	ZG4	ZG4	ZG4	ZG4	ZG4	ZG4
4.	Electrical conductivity	μS cm^{-1}	2760	1300	700	3330	1600	910	3600	1660	980
5.	Ammonia nitrogen	mg l^{-1}	**88.82**	**44.45**	**31.60**	**263.75**	**62.15**	**47.25**	**259.35**	**129.60**	**61.15**
6.	Nitrate nitrogen	mg l^{-1}	0.39	0.19	0.12	1.09	0.54	0.26	1.58	0.88	0.57
7.	o-phosphates	mg l^{-1}	99.6	86.9	59.4	39.4	23.3	32.8	38.4	73.3	97.1
8.	Sulfates	mg l^{-1}	**921.8**	362.0	202.0	**951.0**	272.0	132.0	**794.2**	230.0	95.0
9.	Chlorides	mg l^{-1}	147.5	145	140	35	58	55	20	18	25
10.	Calcium	mg l^{-1}	441	230	142	225.4	196	152	142.1	127	74
11.	Magnesium	mg l^{-1}	76.2	47.6	19.1	178.6	69.1	28.6	88.1	85.73	52.4
12.	Iron	mg l^{-1}	0.97	0.78	0.20	2.10	1.87	0.95	2.43	1.81	1.40
13.	COD $_{KMnO_4}$	mg $l^{-1}O_2$	89.1	56.1	46.1	310.1	112.1	70.1	385.1	144.1	102.1
14.	COD $_{K_2Cr_2O_7}$	mg $l^{-1}O_2$	**330**	**170**	100	**700**	**560**	**280**	**1260**	**680**	**280**
15.	Cu	mg l^{-1}	0.21	0.23	0.15	0.13	0.25	0.29	0.29	0.025	0.30
	Zn		1.22	1.58	1.16	1.93	**3.85**	**4.35**	**3.66**	**4.18**	**5.41**
	Cd		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Ni		0.12	0.07	<0.06	0.12	0.09	0.08	0.18	0.09	0.08
	Pb		0.10	0.13	0.10	0.13	0.26	0.26	0.26	0.26	0.32
	Cr		0.05	0.04	0.04	0.04	0.05	0.06	0.06	0.04	0.05

Table 5. Loads of indices eluted from the fly ash-sludge granulates N 9, N 10, N 14 (single stage test) in [mg kg^{-1} d.m.].

No.	Determined index	Determination value		
		N 9	N 10	N 14
1.	Ammonia nitrogen	888	1506	2314
2.	Nitrite nitrogen	0.17	0.27	0.23
3.	Nitrate nitrogen	4.78	9.40	14.30
4.	o-phosphates	25.0	73.0	167.0
5.	Sulphates	9382	10822	9506
6.	Chlorides	1390	1450	1240
7.	Calcium	3969	3234	4116
8.	Magnesium	1643	119	857
9.	Iron	42.5	17.0	14.0
10.	COD $_{KMnO_4}$	1376	2156	2206
11.	COD $_{K_2Cr_2O_7}$	6500	13800	13000
12.	Cu	1.8	1.6	1.6
	Zn	6.6	10.6	15.3
	Cd	1.3	1.5	1.4
	Ni	0.6	0.6	0.9
	Pb	<0.1	<0.1	<0.1
	Cr	0.4	<0.4	0.4

Table 6. Loads of indices eluted from the fly ash-sludge granulates N 9, N 10, N 14 (tree-stage test) in [mg kg^{-1} d.m.].

No.	Determined index	**Determination value**								
		N 9			N 10			N 14		
		1º	2º	3º	1º	2º	3º	1º	2º	3º
1.	Ammonia nitrogen	888.2	388.9	276.5	2637.5	543.8	413.4	2593.5	1134.0	458.62
2.	Nitrate nitrogen	3.90	1.66	1.05	10.85	4.68	2.27	15.75	7.70	4.28
3.	o-phosphates	996.0	760.4	519.8	394.0	203.9	287.0	384.0	641.4	728.3
4.	Sulphates	9218	3169	1764	9506	2376	1152	7942	2016	710
5.	Chlorides	1475	1269	1225	350	503	481	200	153	188
6.	Calcium	4410	2015	1243	2254	1689	1329	1421	1115	551
7.	Magnesium	762	417	16669	1786	604	250	881	750	393
8.	Iron	9.69	6.84	1.77	20.95	16.33	8.33	24.29	15.83	10.52
9.	COD $_{KMnO_4}$	891	491	403	3101	981	613	3851	1261	766
10.	COD $_{K_2Cr_2O_7}$	3300	1488	875	7000	4900	2450	12600	5950	2100
11.	Cu	2.10	2.01	1.31	1.30	2.19	2.54	2.90	2.19	2.25
	Zn	12.20	13.82	10.15	19.30	33.69	38.06	36.60	36.56	40.57
	Cd	1.20	0.61	<0.53	1.20	0.79	0.70	1.80	0.79	0.60
	Ni	1.00	1.34	0.88	1.30	2.28	2.28	2.60	2.28	2.40
	Pb	<0.10	<0.09	<0.09	<0.10	<0.09	<0.09	<0.10	<0.09	<0.08
	Cr	0.50	0.35	0.35	0.40	0.44	0.53	0.60	0.35	0.38

observed only in the case of the N10 (1:1) granulate extract, i.e. $pH_{1°}$ (7.13)<$pH_{2°}$ (7.17)<$pH_{3°}$ (7.26),

– colour in the range of 60-250 mg $^{-1}$Pt. It was shown that the colour of extracts decreased in subsequent elution stages of the fly ash-sludge mixtures (1°>2°>3°), i.e. the higher the sludge content in the granulate, the stronger the extract colour,

– a very high electric conductivity decreasing in water extracts from subsequent elution stages, i.e. (1°>2°>3°). Moreover, the conductivity increased parallel to the sludge content increase in the granulates, e.g. N $9_{1°}$(2760 µS cm^{-1})<N $10_{1°}$(3330 µS cm^{-1})<N $14_{1°}$ (3600 µS cm^{-1}).

Based on the results from the conducted three-stage elution test (Table 4) the elution loads of the contaminant indices were calculated (Table 6).

The analysis showed that the fly ash-sludge mixtures were characterized by the following parameters:

– high elution level of ammonia nitrogen (in the range of 276.5-2637.5 mg kg^{-1} d.m.) compared to a low level of the eluted nitrate nitrogen (1.05-10.85 mg kg^{-1} d.m.). It is a consequence of a very high ammonia nitrogen concentration in the water extract from each elution stage (Table 4). The permissible value of total nitrogen for effluent discharged to waters and soils is 30 mg N l^{-1} (Table 8),

– a very high elution load of sulphates, in the range of 710-9506 mg kg^{-1} d.m., depending on the type of mixture and elution stage. Similarly as in the case of ammonia nitrogen, sulphate concentrations in the water extracts of the investigated granulates was very high (Table 4); at the same time the permissible value for effluent discharged to waters and soils (500 mg l^{-1}) was exceeded in the water extracts from the first elution stage (Table 8),

– high elution loads of organic compounds determined as dichromate COD. The permissible value of this index for the effluent discharged to waters and soils (150-250 mgO_2 l^{-1}) has been exceeded for granulate N9 in the water extracts of the first, second and third stage of the elution stages (Table 4 and 8).

Analysis of the data in Table 6 allowed us to observe that the loads of the eluted indices decreased in subsequent elution stages with only a few exceptions i.e. metals, o-phosphates and chlorides (these only in granulates N 10 and N 14). In the case of metals the situation was much more complicated since their elution loads in individual elution stages were diversified depending on the type of metal and the fly ash-sludge mixture. A decrease in the subsequent elution stages was observed only in the case of cadmium loads eluted from mixtures N 9, N 10, N 14, nickel loads eluted from mixture N 10 and N 14 and chromium loads eluted from mixture N 9.

Data from the three-stage test allowed us to observe that the elution level of such indices as ammonia nitrogen, nitrate nitrogen, iron, organic compounds determined as COD_{KMnO_4} and $COD_{K_2Cr_2O_7}$ and metals (except for chromium) increased simultaneously to the increase of sludge

Table 7. A comparison of contaminant index loads eluted from the fly ash-sludge granulates N 9, N 10 and N 14 from the single-stage and three-stage elution test [mg kg^{-1} d.m.].

No.	Determined index	Loads of the eluted indices					
		N 9		N 10		N 14	
		Test 1°	Test 3°	Test 1°	Test 3°	Test 1°	
1.	Ammonia nitrogen	888	1554	1506	3595	2314	4186
3.	Nitrate nitrogen	4.78	6.61	9.40	17.80	14.30	27.72
4.	o-phosphates	25.0	2276.1	73.0	884.9	167.0	1753.6
5.	Sulfates	9382	14150	10822	13034	9506	10668
6.	Chlorides	1390	3969	1450	1334	1240	540
7.	Calcium	3969	7669	3234	5272	4116	3087
8.	Magnesium	1643	1346	119	2640	857	2024
9.	Iron	42.5	18.3	17.0	45.6	14.0	50.6
10.	COD_{KMnO_4}	1376	1785	2156	4695	2206	5878
11.	$COD_{K_2Cr_2O_7}$	6500	5663	13800	14350	13000	20650
12.	Cu	1.80	5.45	1.60	6.03	1.60	7.34
	Zn	6.60	36.17	10.60	91.05	15.30	113.74
	Cd	1.30	2.33	1.50	2.69	1.40	3.19
	Ni	0.60	3.12	0.60	5.85	0.90	7.27
	Pb	<0.10	<0.27	<0.10	<0.27	<0.10	<0.26
	Cr	0.40	1.20	<0.40	1.36	0.40	1.32

content in the granulate N 9<N 10<N 14. On the contrary, for such indices as sulphates, chlorides and calcium, their elution level decreased alongside increasing sludge content in the granulates i.e.: N 9>N 10>N 14 (Table 6, 7).

Table 7 presents a comparison of the eluted contaminant indices' loads obtained from the conducted elution tests (single-stage and three-stage). The results clearly indicate that higher loads of eluted contaminants were obtained from the three-stage elution test with only a few exceptions (elution load of magnesium, iron and $COD_{K_2Cr_2O_7}$ from the N 9 mixture, and chloride loads from mixtures N 10 and N 14, calcium load from the N14 mixture). The highest differences were observed in the case of ammonia nitrogen: (N 9: $T_{1°}$ – 888.2 mg kg^{-1} d.m. ≠ $T_{3°}$ – 1553.64 mg kg^{-1} d.m., N 10: $T_{1°}$ – 1506.2 mg kg^{-1} d.m. ≠ $T_{3°}$ – 3594.75 mg kg^{-1} d.m., N 14: $T_{1°}$ – 2313.5 mg kg^{-1} d.m. ≠ $T_{3°}$ – 4186.12 mg kg^{-1} d.m.); o-phosphates (N 9: $T_{1°}$ – 25.0 mg kg^{-1} d.m. ≠ $T_{3°}$ – 2276.12 mg kg^{-1} d.m., N 10: $T_{1°}$ – 73.0 mg kg^{-1} d.m. ≠ $T_{3°}$ – 884.87 mg kg^{-1} d.m., N 14: $T_{1°}$ – 167.0 mg kg^{-1} d.m. ≠ $T_{3°}$ – 1753.62 mg kg^{-1} d.m.) and metals.

Considering the loads obtained from the three-stage test in the multiplicity function of the values obtained in a one-stage test the following regularities can be observed: eluates from all granulates show that the amount of $N\text{-}NH_4$ and $N\text{-}NO_3$ is 300% and 150% respectively higher in the three-stage test when compared to the values obtained in one-stage test. However, the highest difference between one and three-stage tests were found for the amount of o-phosphates eluted (Table 7). Decrease and increase in multiplicity of sulphates, copper and cadmium elution, respectively, along with the increase in amount of sewage sludge in granulates was also observed.

The fertilizing value in terms of biogens elution shows that their level is higher than the permissible values for sewage disposed into water and soil [35]. However, hazard for the water-soil environment will be caused only by a part of biogens not available for plants. So attention should be paid to contents of chlorides, sulphates, heavy metals and zinc mainly because it is eluated in the highest amount; however, its permissible level is exceeded only in the three-stage test.

Conclusions

The conducted investigations provided the basis for formulating the following conclusions:

1. The loads of eluted contamitants depend not only on chemical composition of initial materials, i.e. ashes and sewage sludge, but also on processes occuring in their mixture. In general, the conducted elution tests (one and three-stage) showed the increase in load of eluted contamitants along with the increase in content

Table 8. Maximum permissible values for contamitant [mg l^{-1}] indices acc. to Regulations [35].

No.	Determined index	Maximum permissible concentrations for treated wastes			
		municipal	industrial		
			biodegradable		other
1.	Ammonia nitrogen	10-30*	10-20	30*	n/a
3.	Nitrate nitrogen		30		n/a
4.	Nitrite nitrogen		1		n/a
5.	Total phosphorus	1-5	2-3		3-10
6.	Sulfates	n/a	500		500
7.	Chlorides	n/a	1000		1000
8.	Calcium	n/a	n/a		n/a
9.	Magnesium	n/a	n/a		n/a
10.	Iron	n/a	10		10
11.	COD_{KMnO_4}	n/a	n/a		n/a
12.	$COD_{K_2Cr_2O_7}$	125-150	125-250		125-250
13	Cu	n/a	0.5		0.5
	Zn	n/a	2		2
	Cd	n/a	0.2		0.2
	Ni	n/a	n/a		0.5
	Pb	n/a	n/a		0.5
	Cr	n/a	n/a		1

* N_{total}

of sewage sludge in granulates. However, for the majority of indices it is not a directly proportional dependency. The rate of contaminant release is also caused by chemical binding, precipitation or other effects caused by organic matter or changes in pH values.

2. The load values obtained in the one-stage test and in the first step of the three-stage test can be recognised as comparable, whereas the sum of loads determined in the three-stage test is a differentiated multiplicity of loads determined in the one-stage test. The highest discrepancies were found for o-phosphates. Some regularities were found for elution of nitrogen forms, i.e., total loads of $N\text{-}NH_4$ and $N\text{-}NO_3$ are 3 and 1.5 times higher, respectively, in the three-stage test.
3. In water extracts of all granulates exceedance of the permissible levels of $N\text{-}NH_4$, o-phosphates, sulphates, $COD_{K_2Cr_2O_7}$ and iron for sewage disposed into water and soil according to Regulation [35] was noted. The higher fraction of sewage sludge in granulate the higher exceedance was observed. Sulphates at exceeded levels were released already in the first step of elution, whereas zinc in the entire elution stage, mainly from granulates with share of sewage sludge above 50% (N10 and N14).
4. The most profitable fertilizing properties were demonstrated by the granulate with the highest fraction of sewage sludge (N14). However, due to loads of contaminates eluted it is most hazardous for the soil-water environment among of all analyzed mixtures. The ash-sludge mixture with the same share of sewage sludge and fly ash (N10) was found to be the least hazardous for the environment.

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