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FRACTIONS OF LEAD AND CADMIUM IN SEWAGE SLUDGE COMPOSTED WITH ADDITION OF CALCIUM OXIDE AND POWER STATION ASHES

FRAKCJE OŁOWIU I KADMU W OSADACH ŚCIEKOWYCH KOMPOSTOWANYCH Z DODATKIEM TLENKU WAPNIA I POPIOŁÓW Z ELEKTROWNI

Abstract: This study determined the effect of mixing sludge with calcium oxide, brown coal and hard coal ash and composting the obtained mixtures on the total content and fractions of lead and cadmium isolated by the sequential method. Mixtures of sludge with those components usually contained less lead and cadmium than the sludge itself. Composting usually resulted in a slight increase in the content of heavy metals in sludge and its mixtures with all the components. The content of lead was the highest in the organic (average 54.1 %) and residual (average 33.0 %) fraction in both fresh and composted sludge, with and without all the additions. The content of cadmium was the highest in sludge and their mixtures in the residual (average 59.3 %) and the organic (average 13.2 %) fraction. The content of the most mobile fractions of lead and cadmium fractions (soluble and exchangeable) in the sludge alone as well as in its mixtures with all the components, was rather small and it did not exceed several percent of the whole. The content of lead in the exchangeable fraction which was adsorbed on oxides in the organic and residual fraction was found to increase during the composting process and it was found to decrease in the water-soluble and carbonate fractions. Composting the waste material under study reduced the content of cadmium in the water-soluble and carbonate fraction (adsorbed on oxides) and in the organic fraction, whereas the amounts of the exchangeable and residual fractions increased.

Keywords: sewage sludge, calcium oxide, ash, composting process, lead, cadmium

Introduction

It is common in Poland to use sludge in agriculture as fertiliser. This is economically justifiable because the large amounts of organic matter and biogenous elements which enrich the soil can be put to good use [1]. Agricultural use of sludge has some limitations because of the above-normal content of undesired components, such as

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heavy metals or sanitary contaminations [2]. When introduced to soil, excessive amounts of heavy metals can reduce the yield and lower its quality and, consequently, pose a hazard to consumers. The amount of heavy metals taken up by plants fertilised by sludge depends not only on its amount added to soil, but also on the measures used to relieve the effects of increased content of the elements. Solubility, mobility and the availability to plants of most heavy metals can be reduced by soil liming [3–5]. Sanitation of sludge by mixing it with calcium oxide or substances with high calcium content can be an interesting solution in regard to the phytotoxicity of the elements. Such procedures lead not only to quantitative changes in the heavy metal content, but they can also affect their speciation [6]. Monitoring the hazard that is posed to ecosystems by heavy metals should include determination of their total content, but it should be supplemented by assessment of their mobility based on identification of their species [7, 8].

According to the Regulation of the Minister of Environment on the catalogue of waste [9], by-products of combustion (such as ashes produced by the power industry) are not hazardous products and, as such, they can be used in agriculture. Along with a high content of alkaline compounds, ashes contain large amounts of microelements and heavy metals. The content of heavy metals in ash is not hazardous to plants which are fertilised with them [10].

The aim of the study was to determine the total content of lead and cadmium and their fractions in fresh and composted sludge with the addition of CaO, brown coal ash and hard coal ash, used in the hygienisation of sludge.

Materials and methods

Sludge from mechanical and biological wastewater treatment plants in Siedlce and Lukow, produced as a result of purification of communal waste with a small proportion of industrial sewage, was used in the study. In the technological process in the wastewater treatment plant in Siedlce, sludge is subjected to methane fermentation at the final stage of separation and compaction. Stabilisation of sludge from Lukow was performed under aerobic conditions and the excess water was removed by centrifuging. Organic waste material used in the study contained 18.7 % and 13.8 % of dry matter, respectively. Fresh sludge was mixed separately with CaO, ash from brown coal and ash from hard coal at a 2 : 1 dry matter ratio (w/w). The prepared mixtures were then composted in 200 dm^3 plastic containers for 3 months at a temperature of about 20 ^oC. The compost was stirred every 30 days and samples for examination were taken. Brown coal ash from the third flue gas de-dusting filter in the Patnow CHP plant (burning brown coal from the Belchatow coal mine) contained 17.57 mg Pb and 2.77 mgCd in 1 kg of d.m. Hard coal ash from the PEC power company in Siedlce, contained 74.66 mgPb and 1.30 mgCd in 1 kg of d.m.

The total content of lead and cadmium was determined by the ICP-AES method in stock solutions obtained by dry mineralisation of the materials at the temperature of 450 ^oC. After mineralisation, the ash was poured over with 6 mol $\cdot$ dm^{-3} HCl to decompose carbonates and evaporated to dryness on a sand bath. Subsequently, the chlorides obtained in the process were transferred to volumetric flasks in 10 % hydrochloric acid.

Lead and cadmium fractions were separated by the sequential method (according to Tessier), using the following solutions for extraction in this sequence: H_2O, 1 mol · dm^{-3} $CaCl_2$, 1 mol · dm^3 CH_3COONa, pH ca 5.0, 0.75 mol · dm^{-3} $(NH_4)_2C_2O_4$, pH 3.25, 0.1 mol · dm^{-3} $Na_4P_2O_7$ [11, 12]. Extraction was carried out for 3 hours in centrifuge tubes and the deposit was then centrifuged for 20 minutes at a rotational speed of 5000 rpm. After decantation, before the next extraction solvent was used, the solid phase was washed twice with H_2O, centrifuged (as above) and the relevant stock solution was prepared. Subsequently, all the solutions were mineralised in H_2O_2 and the stock solutions were evaporated to *ca* 5 cm^3. The residue after evaporation was transferred to volumetric flasks in 10 % hydrochloric acid and the content of the heavy metals was determined by the ICP-AES method.

Results and discussion

The lead content in sludge from Lukow (111.35 mg · kg^{-1}) was more than twice higher than in the sludge from Siedlce (51.18 mg · kg^{-1}, Table 1), whereas the content of cadmium in sludge from Siedlce (4.13 mg · kg^{-1}) was higher by nearly 2/3 than in sludge from Lukow (2.65 mg · kg^{-1}, Table 2). The content of the heavy metals in sludge used in the study did not exceed the maximum acceptable content for the substances to be used in agriculture [2].

The addition of CaO to sludge from Siedlce and Lukow produced a mixture with a lower content of lead – 36.6 and 32.9 %, respectively (Table 1). The cadmium content in the sludge with CaO was lower by 39.1 and 44.5 %, respectively, than in the sludge without the addition (Table 2). The addition of brown coal ash to sludge from Siedlce and Lukow produced a mixture with a lower content of lead (23.6 and 29.8 %, respectively) than the sludge without the addition. Mixtures of sludge from Siedlce with brown coal ash contained less cadmium by 8.2 % than the sludge alone, whereas the content of the metal in mixtures of sludge from Lukow with the ash was higher by 12.6 % than in the sludge alone. Mixtures of sludge from Lukow with hard coal ash contained less lead by 10.4 % than the sludge alone, whereas the content of the metal in mixtures of sludge from Siedlce with the ash was higher by 14.1 % than in the sludge alone. The addition of hard coal ash to sludge produced mixtures with a lower content of cadmium (by 22.3 and 16.2 %, respectively) than the sludge without the addition. Composting sludge after methane fermentation, which was later stabilised in aerobic conditions, increased the content of lead by 9.2 and 24.8 %, respectively. Composted mixtures of sludge with CaO, brown and hard coal ash contained more lead by 7.7; 6.1 and 3.8 %, respectively, as compared with its content before composting (average values for sludge from Siedlce and Lukow, Table 3). The total content of cadmium in sludge from Siedlce, after being composted for three months, increased slightly by 4.4 %. The metal content in sludge from Lukow increased as a result of composting by 13.3 % (Table 2). The average content of cadmium in the composted sludge and its mixtures with all the components was slightly higher than in the materials before

Table 1

Total content and fraction of lead in sewage sludge and their mixtures with CaO and ashes, [mgPb · kg^{-1} d.m.]

Kind of sludge	Kind of addition	Before or after composting process	Fraction						Total content
			water-soluble	exchangeable	carbonate	oxide	organic	residual	
Sewage sludge from Siedlce	without addition	fresh	0.575	0.085	1.948	2.590	29.978	16.002	51.177
		composted	0.285	0.000	2.190	3.216	31.914	18.296	55.901
	CaO	fresh	1.197	0.000	3.115	2.801	6.436	18.899	32.447
		composted	1.194	3.668	1.264	2.117	7.813	17.882	33.937
	ash 1^2	fresh	1.370	0.000	3.141	1.663	24.018	8.892	39.083
		composted	0.497	0.000	3.130	2.645	21.854	11.692	39.817
	ash 2^3	fresh	2.241	1.655	2.556	2.795	40.021	9.123	58.390
		composted	1.935	0.000	4.890	3.408	40.532	3.464	54.230
Sewage sludge from Lukow	without addition	fresh	1.121	0.000	4.574	5.246	65.678	34.732	111.350
		composted	1.530	0.000	2.423	5.952	82.702	46.395	139.002
	CaO	fresh	0.744	0.000	1.652	3.055	22.088	47.166	74.703
		composted	0.888	4.602	1.324	3.495	22.167	49.009	81.483
	ash 1^2	fresh	1.439	1.030	2.971	1.873	50.212	20.649	78.180
		composted	0.668	0.000	3.790	3.123	55.354	21.649	84.583
	ash 2^3	fresh	1.472	0.000	3.949	5.778	77.836	10.692	99.727
		composted	0.857	0.000	1.236	4.667	71.500	31.581	109.840
Averages for additives		without addition	0.878	0.021	2.784	4.251	52.568	28.856	89.358
		CaO	1.006	2.068	1.839	2.867	14.626	33.239	55.643
		ash 1^2	0.994	0.258	3.258	2.326	37.860	15.721	60.416
		ash 2^3	1.626	0.414	3.158	4.162	57.472	13.715	80.547
$LSD_{0.05}$			0.171	1.609	0.522	0.367	5.820	3.773	3.828

Ash 1^2 – ash from brown coal, ash 2^3 – ash from pit-coal.

Table 2

Total content and fraction of cadmium in sewage sludge and their mixtures with CaO and ashes, mg Cd · kg^{-1} d.m.

Kind of sludge	Kind of addition	Before or after composting process	Fraction						Total content
			water-soluble	exchangeable	carbonate	oxide	organic	residual	
Sewage sludge from Siedlce	without addition	fresh	0.076	0.419	0.265	0.225	0.534	2.609	4.128
		composted	0.077	0.253	0.152	0.309	0.421	3.096	4.308
	CaO	fresh	0.079	0.050	0.129	0.381	0.333	1.541	2.513
		composted	0.061	0.212	0.171	0.216	0.262	1.645	2.567
	ash 1^2	fresh	0.069	0.282	0.406	0.090	0.234	2.707	3.788
		composted	0.098	0.313	0.327	0.167	0.420	2.590	3.915
	ash 2^3	fresh	0.250	0.519	0.557	0.096	0.478	1.308	3.208
		composted	0.114	0.685	0.420	0.081	0.282	1.980	3.562
Sewage sludge from Lukow	without addition	fresh	0.122	0.120	0.078	0.240	0.562	1.531	2.653
		composted	0.063	0.036	0.058	0.264	0.611	1.975	3.007
	CaO	fresh	0.039	0.101	0.071	0.283	0.285	0.694	1.473
		composted	0.054	0.213	0.012	0.128	0.292	0.805	1.504
	ash 1^2	fresh	0.025	0.198	0.192	0.151	0.379	2.042	2.987
		composted	0.026	0.472	0.356	0.109	0.163	1.865	2.991
	ash 2^3	fresh	0.072	0.326	0.296	0.148	0.389	0.992	2.223
		composted	0.059	0.302	0.281	0.135	0.223	1.221	2.221
Averages for additives		without addition	0.085	0.207	0.138	0.260	0.532	2.303	3.524
		CaO	0.058	0.144	0.096	0.252	0.293	1.171	2.014
		ash 1^2	0.055	0.316	0.320	0.129	0.299	2.301	3.419
		ash 2^3	0.124	0.458	0.389	0.115	0.343	1.375	2.803
$LSD_{0.05}$			0.011	0.039	0.035	0.021	0.041	0.208	0.307

Ash 1^2 – ash from brown coal, ash 2^3 – ash from pit-coal.

Table 3

The average of total content and fraction of lead [mg · kg^{-1} d.m.] in sewage sludge for kind of sludge as well as for composting process

Studied factors		Fraction						Total content
		water-soluble	exchangeable	carbonate	oxide	organic	residual	
Kind of sewage sludge	from Siedlce	1.162	0.676	2.779	2.654	25.321	13.031	45.623
	from Lukow	1.090	0.704	2.740	4.149	55.942	32.734	97.359
	$LSD_{0.05}$	n.i.	n.i.	n.i.	0.195	3.094	2.006	2.035
Composting process of sludge	fresh sludge	1.270	0.346	2.988	3.225	39.533	20.769	68.132
	composted sludge	0.982	1.034	2.531	3.578	41.730	24.996	74.849
	$LSD_{0.05}$	0.091	0.655	0.173	0.195	n.i.	2.006	2.035

n.i. – differences not important.

Table 4

The average of total content and fraction of cadmium [mg · kg^{-1} d.m.] in sewage sludge for kind of sludge as well as for composting process

Studied factors		Fraction						Total content
		water-soluble	exchangeable	carbonate	oxide	organic	residual	
Kind of sewage sludge	from Siedlce	0.103	0.342	0.303	0.196	0.371	2.185	3.499
	from Lukow	0.058	0.221	0.168	0.182	0.363	1.391	2.382
	$LSD_{0.05}$	0.006	0.021	0.018	0.011	n.i.	0.110	0.163
Compos-ting process of sludge	fresh sludge	0.092	0.252	0.249	0.202	0.399	1.678	2.871
	composted sludge	0.069	0.311	0.222	0.176	0.334	1.897	3.009
	$LSD_{0.05}$	0.006	0.021	0.018	0.011	0.023	0.110	n.i.

composting, but the difference was not statistically significant (Table 4). The effect of a slight increase in lead and cadmium content in the organic and mineral-organic materials under study was caused by mineralisation of the organic matter contained in them.

Organic fraction accounted for the highest part of lead content in fresh sludge: 58.6 % in sludge from Siedlce and 59.0 % in sludge from Lukow (Table 1, Fig. 1). About 1/3 (31.2 %) of the total content of lead in the sludge was in the fraction which was unextractable by the reagents used in the experiment, *ie* in the extraction residue. The proportion of lead in the water soluble, exchangeable, carbonate and oxide fraction was small and equal to: 1.0, 0.04, 4.0 and 4.8 %. Residual fraction (63.2 % in sludge from Siedlce and 57.7 % in sludge from Lukow [Table 2, Fig. 2]), contained the highest proportion of cadmium in fresh sludge. It was followed by the organic fraction, which accounted for 12.9 and 21.2 % of sludge from Siedlce and Lukow, respectively. The proportion of the most mobile fractions, *ie* the water-soluble and exchangeable fractions, in the total cadmium content, was equal to 1.8 % and 10.2 % in sludge from Siedlce and 4.6 and 4.5 % in sludge from Lukow. The carbonate and oxide fractions accounted for 11.9 % each of the total cadmium content, both in sludge from Siedlce and from Lukow. The results confirm the thesis that a small part of the total content of heavy metals is present in mobile fractions, but they usually form combinations with the organic and aluminosilicate fractions [13]. However, the mobility of cadmium contained in sludge is higher compared with other heavy metals [14, 15].

The addition of CaO to sludge from Siedlce and from Lukow increased to the largest extent the portion of the lead fraction which could be extracted with the reagents used, *ie* from 31.2 to 61.7 % of its total content. The portion of the exchangeable, carbonate fraction and that adsorbed on oxides increased to 1.8, 4.5 and 5.5 %, respectively. After CaO was added to sludge, exchangeable lead was not determined in it, and the portion

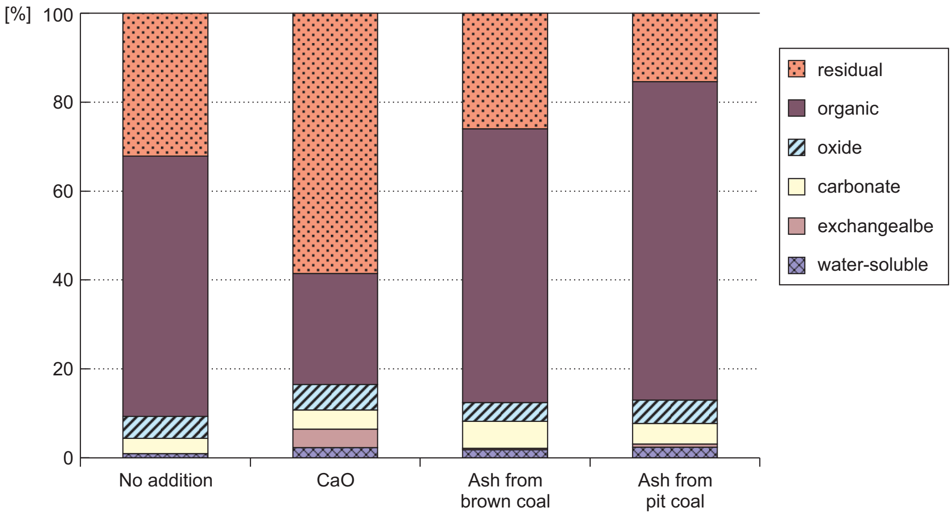

Fig. 1. The proportional part [%] of lead fractions in sewage sludge depending on additives to them

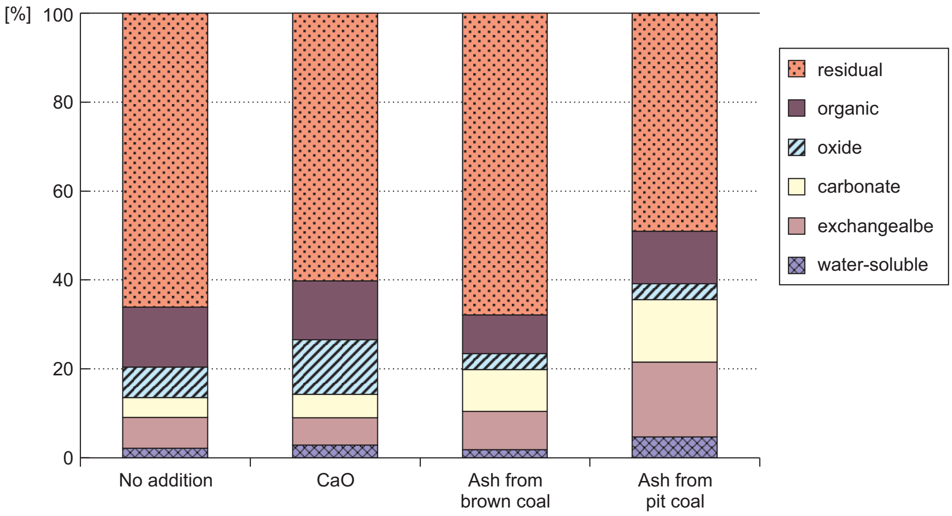

Fig. 2. The proportional part [%] of cadmium fractions in sewage sludge depending on additives to them

of the organic fraction decreased by more than a half, *ie* to 26.6 % of the total content. No considerable changes in the portion of each lead fraction in its total content were observed after brown and hard coal ash were added to sludge. The portion of lead in water-soluble, exchangeable and carbonate fraction increased slightly and that in the residual fraction decreased. After CaO was added to both types of sludge, the portion of oxide fraction of cadmium increased from 7.2 to 17.2 %. At the same time, the portion of residual fraction decreased from 60.5 to 54.2 %. After CaO was added to sludge from Siedlce, the portion of exchangeable fraction decreased considerably, from 10.2 to 2.0 %. Different results were presented by Szymanski and Janowska [16], who stabilised sludge with lime and observed an increase in heavy metal content in the ion-exchange fraction and increase in the organic matter mineralisation rate, which resulted in formation of their mobile species. The portion of water-soluble, carbonate and organic fraction of cadmium did not change considerably after CaO was added to the sludge under study. After brown coal ash was added to sludge from Siedlce, the portion of the exchangeable, oxide and organic fractions decreased, whereas the portion of carbonate and residual fractions increased. After the same ash was added to sludge from Lukow, the portion of the water-soluble, oxide and organic fractions decreased, whereas the portion of exchangeable, carbonate and residual fractions increased. After hard coal ash was added to sludge from Siedlce, the portion of water-soluble, exchangeable and carbonate fractions increased, whereas the portion of oxide and residual fractions decreased. Mixtures of sludge from Lukow with hard coal ash contained smaller portions of water-soluble, oxide, organic and residual fractions and larger portions of exchangeable and carbonate fractions than in sludge alone. Research conducted by Rosik-Dulewska [6] found a small portion of mobile fractions of lead and cadmium in sludge with an addition of mineral waste. The elements are bound to poorly-soluble fractions, with limited availability to plants.

The content of lead in the exchangeable fraction (one which was adsorbed on oxides, in the organic and residual fraction) was found to increase as a result of composting sludge and its mixtures with brown and hard coal ash and it was found to decrease in the water-soluble and carbonate fractions (Table 3). The portion of cadmium in the exchangeable and residual fraction increased, whereas its amount decreased in the fractions: water-soluble, carbonate, adsorbed on oxides and organics (Table 4). The results of this experiment and literature data on forms in which heavy metals occur in fresh and composted sludge and its mixtures with CaO and with mineral waste with high calcium content, *eg* with power plant ash, suggest a low hazard to the environment posed by the presence of lead and cadmium as the elements are present as species of low mobility [6, 15, 17, 18].

Conclusions

1. The addition of power plant ash to sludge in most cases resulted in a decrease in lead and cadmium content in the mixtures.
2. The largest portions of lead and cadmium in sludge with no additions and in mixtures with CaO and brown and hard coal ash were present in organic and residual (unextractable) fractions. The content of mobile species of cadmium was small.
3. The addition of power plant ash to sludge in most cases resulted in an increase in lead and cadmium content in the exchangeable and carbonate fractions and in a decrease in their content in the oxide, organic and residual fractions. The addition of CaO usually increased the portion of the oxide fraction and decrease the organic fraction of the elements.
4. Composting increased the portions of lead and cadmium in sludge with no additions and in mixtures with CaO and brown and hard coal ash. However, the portions of water-soluble and carbonate fractions decreased, whereas the portion of exchangeable and residual fractions of the heavy metals under study increased.

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FRAKCJE OŁOWIU I KADMU W OSADACH ŚCIEKOWYCH KOMPOSTOWANYCH Z DODATKIEM TLENKU WAPNIA I POPIOŁÓW Z ELEKTROWNI

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Abstrakt: Określono wpływ mieszania osadów ściekowych z tlenkiem wapnia, popiołem z węgla brunatnego i kamiennego oraz kompostowania otrzymanych mieszanin na zawartość całkowitą oraz frakcje ołowiu i kadmu wydzielone sekwencyjnie. Mieszaniny osadów ściekowych z wymienionymi komponentami zawierały najczęściej mniej ołowiu i kadmu niż same osady. W trakcie kompostowania stwierdzono na ogół niewielkie zwiększenie się zawartości badanych metali ciężkich w osadach ściekowych i ich mieszaninach ze wszystkimi komponentami. Zarówno w świeżych, jak i w kompostowanych osadach ściekowych bez dodatku i ze wszystkimi dodatkami, największy udział stanowił ołów we frakcji organicznej (średnio 54.1 %) i rezydualnej (średnio 33.0 %). Kadm w największej ilości występował w osadach ściekowych i ich mieszaninach we frakcji rezydualnej (średnio 59.3 %) oraz frakcji organicznej (średnio 13.2 %). W samych osadach ściekowych, a także w ich mieszaninach ze wszystkimi komponentami udział frakcji ołowiu i kadmu o największej mobilności (rozpuszczalnej w wodzie i wymiennej) był niewielki i nie przekraczał kilkunastu procent całkowitej zawartości. W trakcie kompostowania osadów ściekowych i ich mieszanin stwierdzono zwiększenie ilości ołowiu we frakcji wymiennej, zaadsorbowanej na tlenkach, organicznej i rezydualnej, natomiast zmniejszyła się ilość frakcji rozpuszczalnej w wodzie i węglanowej. Kompostowanie badanych materiałów odpadowych zmniejszyło ilość kadmu występującej we frakcji rozpuszczalnej w wodzie, węglanowej, zaadsorbowanej na tlenkach i organicznej, natomiast zwiększeniu uległa ilość frakcji wymiennej i rezydualnej.

Słowa kluczowe: osady ściekowe, tlenek wapnia, popiół, kompostowanie, ołów, kadm