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SANITATION OF WASTEWATER SLUDGE WITH MINERAL WASTES AS METALS SPECIATION FORMS

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SANITACJA OSADÓW ŚCIEKOWYCH MINERALNYMI SUROWCAMI ODPADOWYMI A FORMY SPECJACYJNE METALI

Właściwe przeprowadzenie higienizacji osadów ściekowych mimo wielu – głównie teoretycznych – możliwości ciągle stwarza problem w kontekście ich przyrodniczego zastosowania. Dlatego też poszukuje się coraz to nowych rozwiązań w tym zakresie. Jedną ze stosowanych dotychczas metod higienizacji osadów ściekowych jest wapnowanie, jest to jednak metoda dość droga.

Poszukiwanie substytutu o dużej zawartości wapnia, a przy tym nietoksycznego dla środowiska doprowadziło do badań nad wykorzystaniem w tym celu mineralnych surowców odpadowych (MSO), tzn. popiołów energetycznych z półsuchego odsiarczania spalin w Elektrowni „Opole".

Popiół mieszano z osadem ściekowym (po wirówce) w różnych proporcjach. Po trzech dniach analizowane mieszanki poddano badaniom mikrobiologicznym. Wyniki badań wykazały skuteczność przeprowadzonej sanitacji, a tym samym wskazały na mikrobiologiczną przydatność osadów do przyrodniczego wykorzystania. Badania chemizmu mieszanek MSO z osadem oraz prób kontrolnych (tzn. osadu i MSO) ukierunkowano na określenie całkowitej zawartości metali ciężkich oraz na rozdział poszczególnych metali między wyodrębnione frakcje.

Na podstawie przeprowadzonych badań stwierdzono, że po dodaniu MSO do osadów ilość metali związanych we frakcjach biogennych (frakcja I – II) nie uległa istotnym zmianom. Kadm, cynk i częściowo chrom związane są z frakcją tlenków żelaza i manganu (frakcja III), która wrażliwa jest na zmiany potencjału redox. We frakcji tej nie zauważa się istotnej zmiany zawartości wraz ze wzrostem udziału osadu czy MSO. We wszystkich analizowanych próbach z frakcją organiczną (frakcja IV) w największych ilościach związane są miedź i chrom, natomiast w pozostałości (frakcja V) związane są głównie kadm, nikiel i ołów.

Reasumując stwierdzić należy, że wprowadzenie do gleby mieszanek osadu z MSO, w dowolnej proporcji, nie spowoduje zwiększenia zagrożenia metalami ciężkimi. Przeprowadzone badania specjacji metali osadów ściekowych oraz ich mieszanek z MSO wskazują na podobny rozdział metali w poszczególnych frakcjach, a najbardziej niebezpieczne dla gleb, wód i roślin metale ciężkie, takie jak ołów, chrom, nikiel oraz kadm i cynk, związane są we frakcjach słabo rozpuszczalnych, a tym samym słabo dostępnych dla ekosystemu.

Summary

Despite many technological possibilities, proper sanitation of sludge creates problems to their natural use. Thus, new solutions are still being looked for.

Liming is one of the methods for sludge sanitation, however, rather expensive one.

Seeking the substitute of high calcium content and non-toxic for environment has led to investigations on the application of mineral wastes – ashes from semi-dry sulfur removal from flue gases in the "Opole" power plant for sludge sanitation purposes.

Ash was mixed with sludge in various proportions. After 3 days, the microbiological exams of the mixtures were carried out. The investigation data proved the performed sanitation effective and confirmed microbiological usability of the sludge for a natural use.

The total contents of heavy metals and their distribution between particular fractions were determined in the sludge mixtures with mineral waste and in reference samples (i.e. sludge and mineral waste).

No significant changes of metals proportion bound with biogenic fractions (fractions I–II) after addition of the mineral wastes to sludge were observed.

Cadmium, zinc and partially chrome are bound with the iron and manganese oxides fraction (fraction III) which is sensitive to the redox potential changes. No significant change of contents was observed with the increase in a contribution of sludge or mineral waste.

In all samples of the organic fraction (fraction IV) chrome and copper are bound in the highest amounts, and in the residue fraction (fraction V) cadmium, nickel and lead are bound, mainly.

The investigation has showed that addition of optional proportions of sludge and mineral wastes mixtures into soil did not result in increase in heavy metals hazard. The investigation of the metals speciation in sludge and their mixtures with the mineral wastes showed similar metals distribution in individual fractions. The most hazardous elements for soil, water and plants such as lead, chrome, nickel, cadmium and zinc are bound in slightly soluble fractions and thus are hardly available to the ecosystem.

INTRODUCTION

There are many methods for sanitation of sludge from municipal wastewater treatment plants known in literature and in practice [1, 2, 7, 8, 10–12]. Nevertheless, the search for new methods which would be more effective and cheaper has been continued.

Mineral waste rich in lime such as fly ash can serve as a substitute of lime used for sanitation of wastewater sludge.

Interest in ash application for the above mentioned purposes shows J. Sawa [8] who carries out research on modification of wastewater sludge to improve its dehydration and mechanical properties, reduction of chemical pollutants leaching, reduction of sludge percolation and proper sanitation effectiveness. In the first phase of his investigations, the author analyzed the impact of selected modifiers on the mechanical and organic properties of leaching. The collected data shows that, beside others, fly ash serves as a good component to modify the aforementioned properties of sludge before its use for non-industrial purposes.

GOAL OF THE STUDY AND APPLIED METHODS

The goal of the study was to investigate whether and in what time after mixing with ash from dry desulphurisation of flue gas the sanitation of sludge occurs.

For the research the sludge from the Municipal Wastewater Treatment Plant in Opole was used. The sludge was sampled immediately after dehydration on centrifuge separator. The fly ash from dry desulphurisation was sampled from the Opole Power Plant.

Ash was mixed with wastewater sludge in proportions 1:1, 1:2, 1:4, 1:5. After three days the mixtures were microbiologically examined.

QUANTITATIVE DETERMINATION OF TOTAL HEAVY METAL CONTENT IN SLUDGE

Quantitative determination was carried out in samples prepared in compliance with the standard: BN-64/6215-17, using the method with *aqua regina* (a method recommended by the Polish Institute of Crops, Fertilization and Soil Sciences – Instytut Upraw, Nawożenia i Gleboznawstwa). In the case of ash, mineralization was carried out in the mixture of nitric and perchloric acid. Concentration measurements were made by methods of Perkin Elmer Atomic Absorption Spectrometer Model 1100 B-Operator Manual" 1982.

QUALITATIVE DETERMINATION OF HEAVY METALS – SPECIATION ANALYSIS

Fractionation of wastewater sludge and its mixtures was carried out using Tessier's sequential chemical extraction procedure [13]. The goal of the fractionation was to extract five (Cd, Cr, Cu, Ni, Pb, Zn) heavy metal fractions:

fraction I – exchangable metals;
fraction II – metals bound with carbon;
fraction III – metals bound with iron and manganese oxides;
fraction IV – metals bound with organic matter;
fraction V – residual bound with silicates.

Analysis of water extracts of individual fractions was made by atomic absorption spectrometry (AAS).

RESEARCH RESULTS

Due to the fact that the primary goal of the research was to identify if and in what time sanitation of wastewater sludge occurs, after three days of its mixing with fly ash from dry desulfurization of flue gas, the sludge was microbiologically examined. The data from the tests is presented in Table 1 below.

The results were evaluated in compliance with the guidelines of the Institute for Rural Medicine (Instytut Medycyny Wsi) in Lublin issued in 1986 ("Methods for the control of wastewater sludge sanitary state").

Among the bacteriologically examined samples only the 0 sample i.e. pure sludge did not meet the standards set up for sludge application for natural use.

Table 1. Results of physical, bacteriological and parasitological examination of wastewater sludge and mixture of sludge with fly ash (23. March, 1997)*

Specification	Sample 0	Sample 1	Sample 2	Sample 4	Sample 5
Ash: sludge	sludge	1:1	1:2	1:4	1:5
Coliforms Index	0.000001g in dry mass	> 1.5 g in dry mass	> 1.5 g dry mass	> 1.5 g dry mass	> 1.5 g dry mass
Fecal Coliforms Index	0.00003 g dry mass	> 1.5 g dry mass	> 1.5 g dry mass	> 1.5 g dry mass	> 1.5 g dry mass
Clostridium perfringens index	0.0001 g dry mass	0.001 g dry mass	0.001 g dry mass	0.001 g dry mass	0.0001 g dry mass
Salmonella bacillus in 20 g	Salmonella bracuderup	Not found	Not found	Not found	Not found
Ascaris lumbricoides and Trichocephalus trichiura eggs	Not found	Not found	Not found	Not found	Not found
Sludge humidity	69.5 %	27.6 %	38.5 %	40.4 %	58.6 %
pH	7.0	11.62	11.43	11.0	10.92

* The above presented tests were performed in the District Sanitary and Epidemiological Station in Opole.

The other samples – mixtures of sludge and fly ash (samples 1, 2, 4 and 5), met the above mentioned sanitary standards. Parasite eggs were not determined in any of the tested samples.

The research data proves that application of fly ash from flue gas desulphurisation to sanitation of wastewater sludge brings desired effects, while, at the same time results in sludge enrichment in a new portion of trace elements in that heavy metals.

A complete chemical analysis of the fly ash used for the investigations was carried out. The table below comprises only these metals which must be obligatorily determined in sludge to be applied for natural use.

The content of heavy metals determined in fly ash (see Table 2) is comparable to the amount determined in pure wastewater sludge, except for nickel whose content is significantly higher in ash, as well as zinc and lead whose content is higher in the analyzed sludge.

Total heavy metal content both in wastewater sludge and in its mixture with fly ash meets the standards of UE and the guidelines of the Institute of Environmental Protection [14] set up for sludge used for non-industrial purposes (i.e. in agriculture, for land reclamation for agricultural purposes, compost production, land reclamation for non-agricultural purposes, for cultivation of crops used for compost production and for land fixation with plants).

Based on own research data as well as investigations carried out by other authors [3–7], it can be stated that determination of a total content of a specific elements does not provide information sufficient enough as to determine its toxicity, bioavailability, cumulating, migration etc. as these properties depend upon the physical and chemical form in which it occurs. One of

Table 2. Total content of heavy metals in fly ash from flue gas dry desulphurisation, in wastewater sludge and in the mixtures of both in [mg/kg]

Fly ash: sludge	Cd	Cr	Cu	Ni	Pb	Zn
Fly ash	4.0	123.3	165.8	57.8	66.0	127.3
Sludge	3.0	119.0	145.0	18.50	92.0	1470.0
1:1	2.0	76.0	91.5	19.5	96.5	755.5
1:2	2.0	72.0	98.0	20.5	62.0	660.0
1:4	2.5	79.5	116.5	15.5	74.5	975.0
1:5	3.5	101.0	127.0	18.0	82.5	1185.0
Permissible standard*	10	500	800	100	500	2500

* The highest permissible heavy metal content in sludge used for agricultural purposes.

techniques used for extraction of individual fractions is the sequential extraction procedure which consists in multiple extraction of the analyzed sample with specific agents of differentiated leaching potential. Afterwards metal content in prepared extracts is determined.

In order to determine the risk which the introduction of wastewater sludge and fly ash mixture into environment may result in, a speciation analysis was carried out. The analysis allowed for speciation the forms of metals we are interested in and their quantitative determination.

Graphs 1–6 and table 3 present the data from the speciation analysis of metals.

Based on the analysis of the data obtained in the course of investigations and presented in the graphs it can be stated that regardless of sludge proportions added to fly ash, the volume of metals bound in all biogenic fractions (fraction I–II) did not change significantly and is the lowest in the case of lead, zinc, cadmium and copper, and only slightly increased in the case of chromium and nickel in sludge-ash mixture 1:5.

At raising proportion of wastewater sludge to ash (4:1 and 5:1) an increase of chromium mobility has been observed, similarly as in the case of pure wastewater sludge analytics [3–7].

Zinc, both in pure sludge and in sludge mixtures is bound mainly with manganese and iron oxides fraction (fraction III), which is sensitive to redox potential changes. Also Cd, Cr and Ni are much more bound with this fraction than with fraction I and II. In the case of fraction III, except for zinc, no specific relation between the increase of metal content along with the increase of sludge or ash proportion was observed.

Mainly copper, then chromium, lead and other analysed metals are bound with the organic fraction (fraction IV). It was noted that the higher the proportion of sludge in mixture, the higher the copper and chromium content bound with fraction IV.

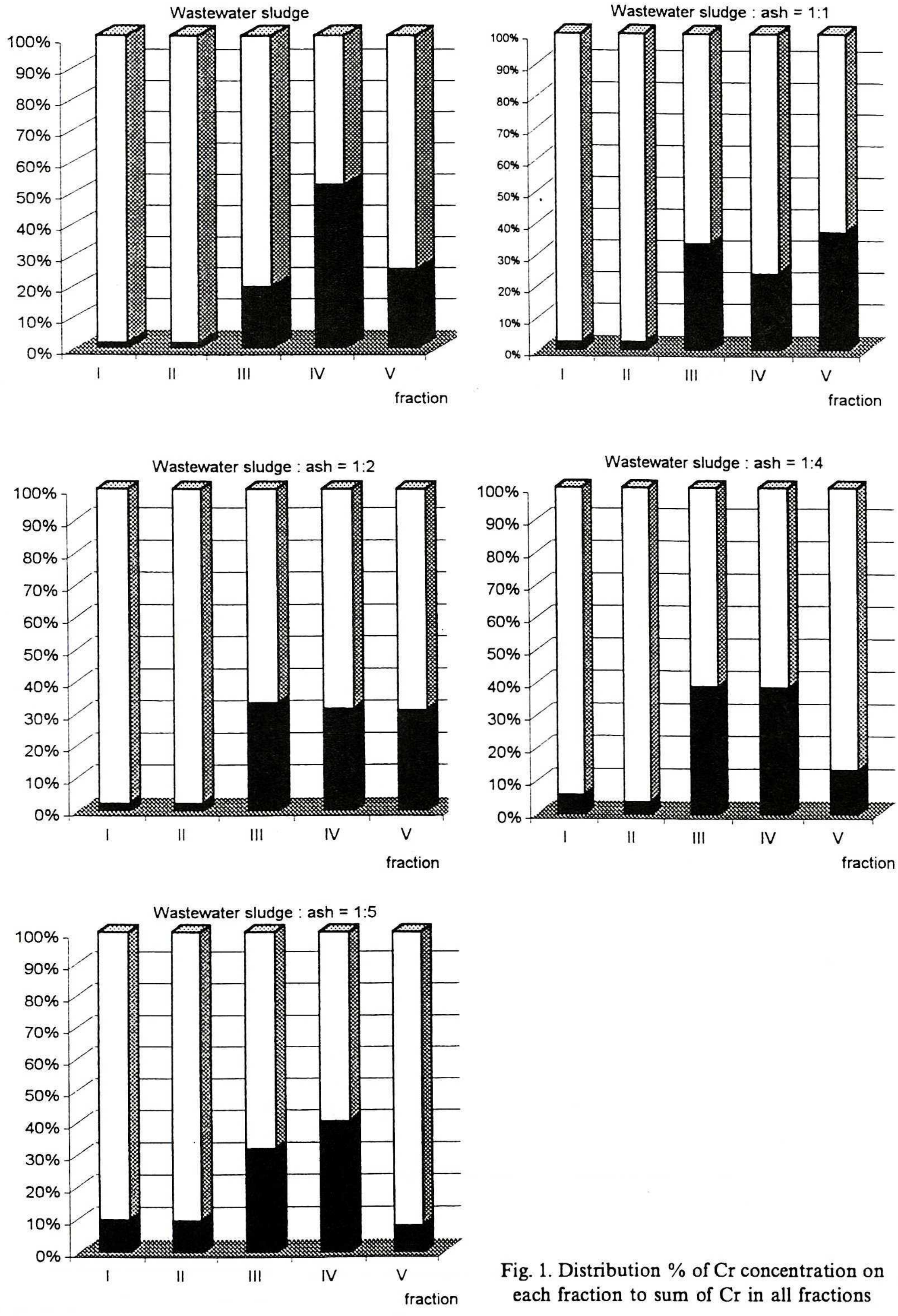


Fig. 1. Distribution % of Cr concentration on each fraction to sum of Cr in all fractions

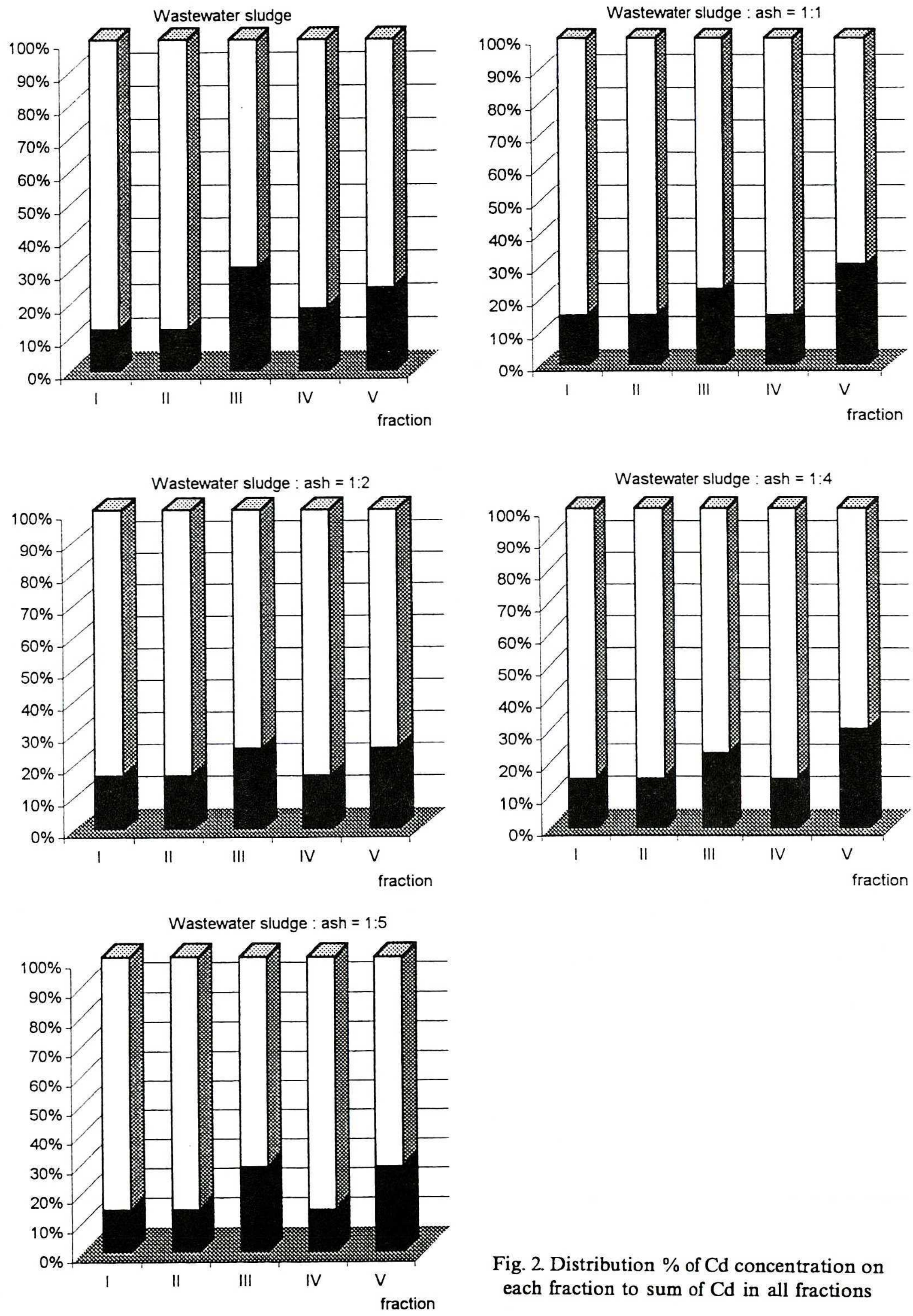
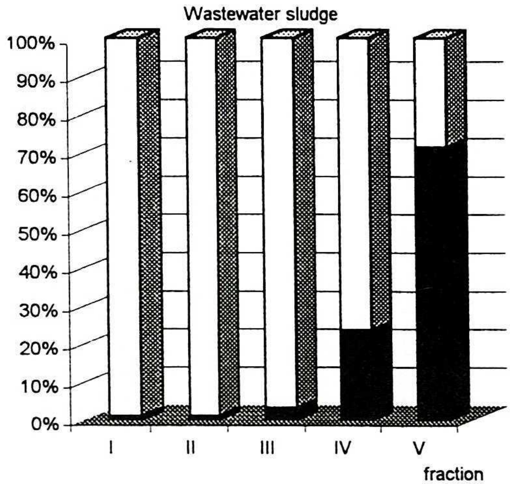
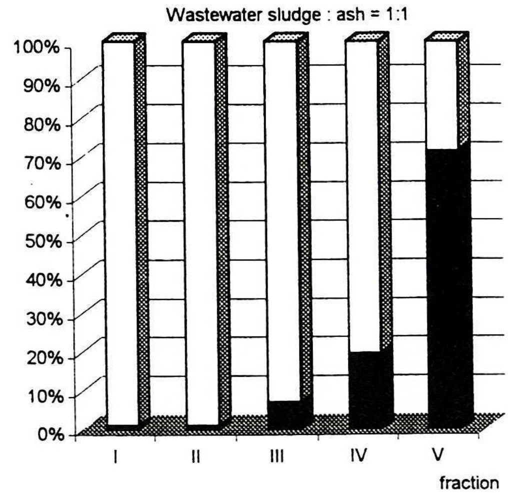
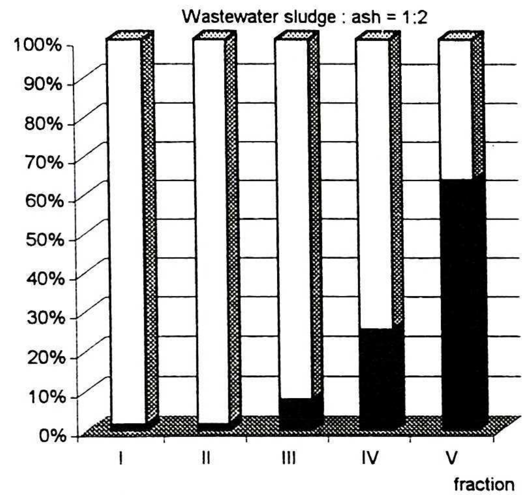
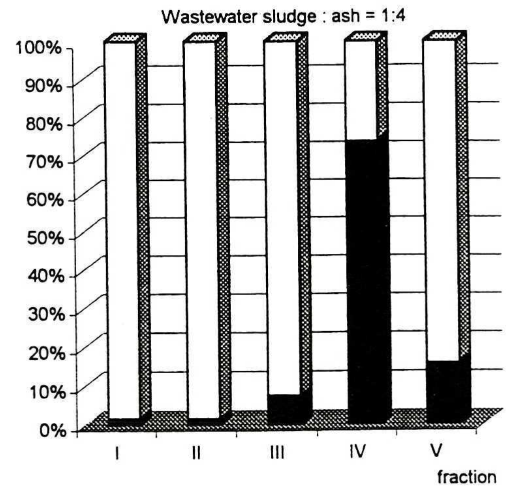


Fig. 2. Distribution % of Cd concentration on each fraction to sum of Cd in all fractions









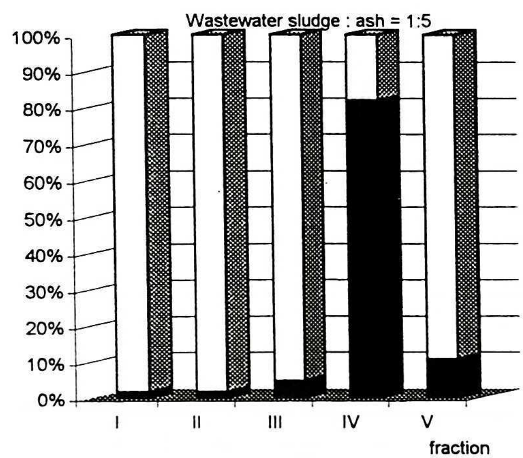
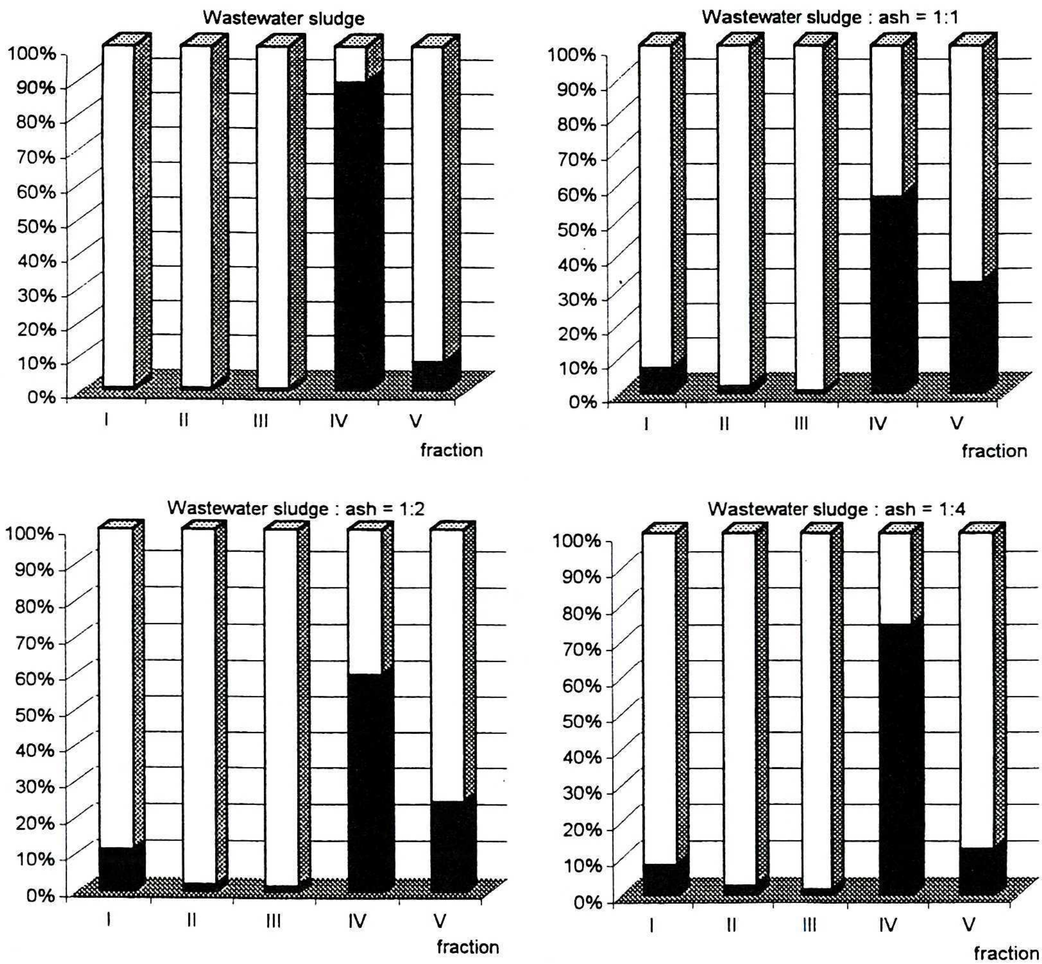


Fig. 3. Distribution % of Pb concentration on each fraction to sum of Pb in all fractions



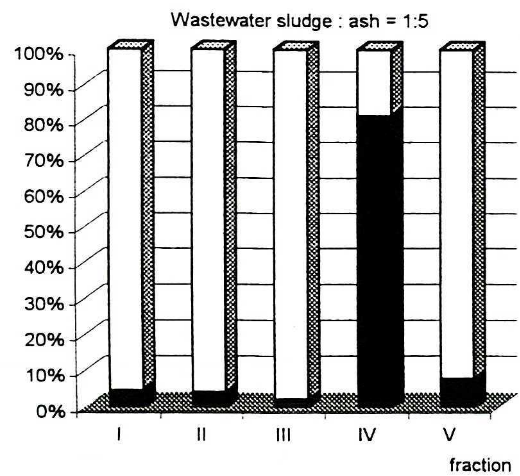
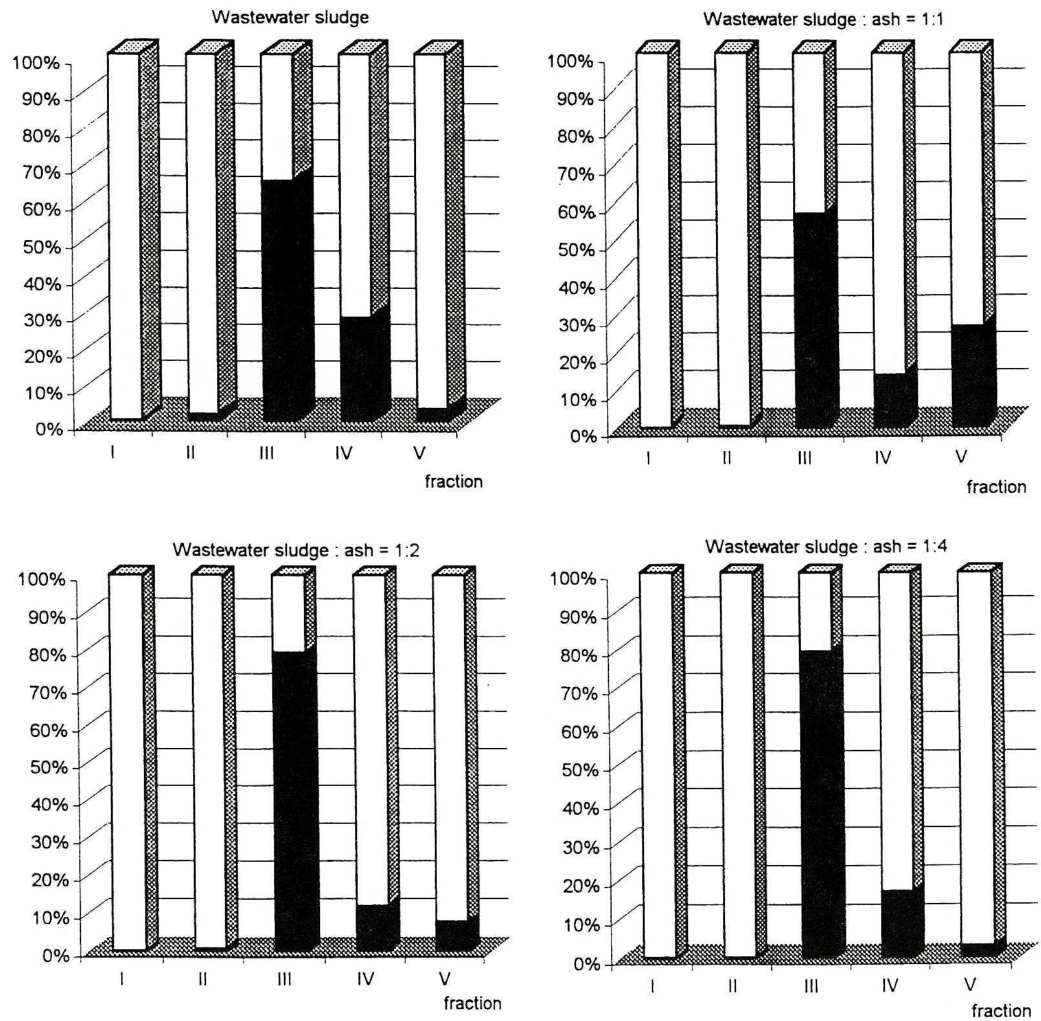


Fig. 4. Distribution % of Cu concentration on each fraction to sum of Cu in oll fractions



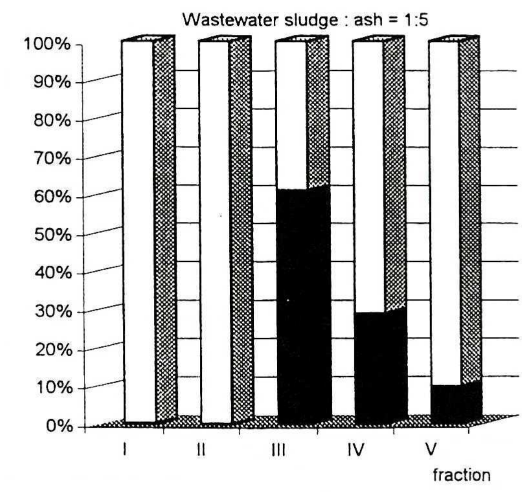
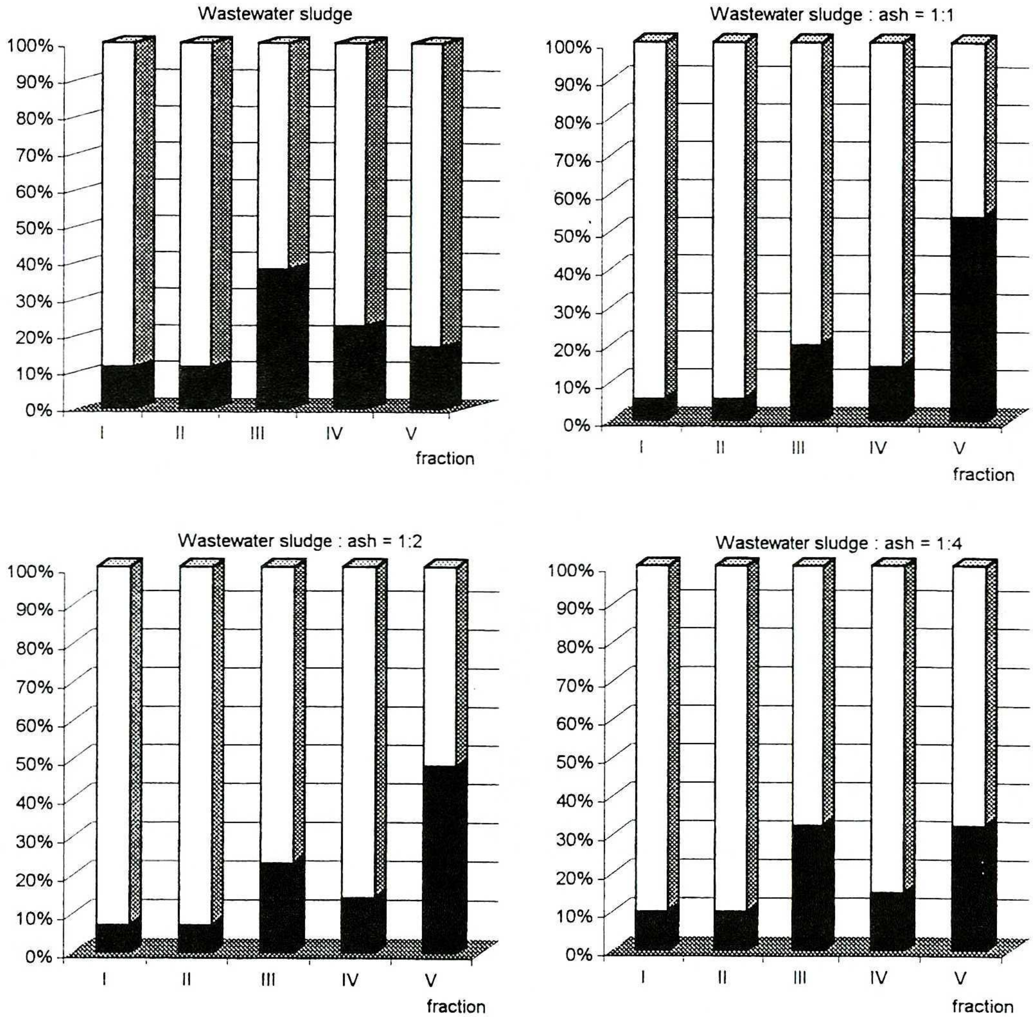


Fig. 5. Distribution % of Zn concentration on each fraction to sum of Zn in all fractions



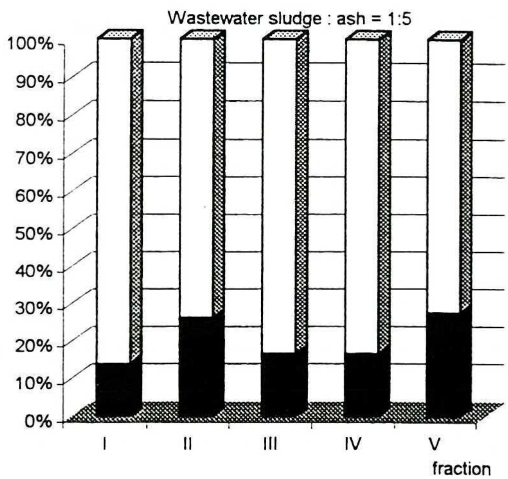


Fig. 6. Distribution % of Ni concentration on each fraction to sum of Ni in all fractions

Table 3. Results of heavy metal speciation analysis in wastewater sludge and its mixture with fly ash

No.	Fraction	Heavy metal content [mg/kg of dry mass] and [% of total content]												Comments
		Cd		Cr		Cu		Ni		Pb		Zn		
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	
1.	I	0.999	12.49	1.999	1.42	0.999	0.61	1.999	11.26	0.999	0.84	3.998	0.30	Sludge
2.	II	0.999	12.49	1.999	1.42	0.999	0.61	1.999	11.26	0.999	0.84	26.5	1.99	
3.	III	2.5	31.26	27.5	19.57	0.999	0.61	6.75	38.03	3.75	3.16	873.0	65.51	
4.	IV	1.50	18.75	73.5	52.31	147.5	89.67	4.0	22.54	28.0	23.63	382.0	28.66	
5.	V	2.0	25.01	35.5	25.26	14.0	8.51	3.0	16.90	84.75	71.52	47.2	3.54	
6.	I	0.99	15.30	2.0	2.43	8.48	7.59	2.0	5.77	0.99	0.92	0.99	0.14	1:1
7.	II	0.99	15.30	2.0	2.43	2.49	2.23	2.0	5.77	0.99	0.92	4.74	0.65	Fly ash:
8.	III	1.5	23.18	27.7	33.66	0.99	0.89	6.98	20.14	7.49	6.98	418.5	57.40	sludge
9.	IV	0.99	15.30	19.9	24.18	63.6	56.91	4.98	14.37	20.95	19.53	104.8	14.37	
10.	V	2.0	30.91	30.7	37.30	36.2	32.39	18.7	53.95	76.85	71.64	200.0	27.43	
11.	I	0.99	16.58	2.0	2.02	14.5	11.53	2.0	7.15	0.99	1.48	0.99	0.15	1:2
12.	II	0.99	16.58	2.0	2.02	2.49	1.98	2.0	7.15	0.99	1.48	4.74	0.70	Fly ash:
13.	III	1.5	25.13	33.2	33.48	2.0	1.59	6.49	23.20	5.24	7.83	538.5	79.55	sludge
14.	IV	0.99	16.58	31.2	31.48	75.6	60,10	3.98	14.23	17.0	25.42	80.8	11.94	
15.	V	1.50	25.13	30.75	31.01	31.2	24.80	13.5	48.27	42.65	63.78	51.9	7.67	
16.	I	0.99	15.30	5.0	5.57	8.24	8.37	2.0	10.00	0.99	1.48	1.25	0.13	1:4
17.	II	0.99	15.30	3.0	3.34	2.50	2.54	2.0	10.00	0.99	1.48	0.99	0.11	Fly ash:
18.	III	1.50	23.18	35.0	39.00	1.50	1.52	6.5	32.52	5.0	7.50	734.5	79.58	sludge
19.	IV	0.99	15.30	34.75	38.72	73.7	74.87	3.0	15.01	49.2	73.78	157.5	17.06	
20.	V	2.0	30.91	12.0	13.37	12.5	12.70	6.49	32.47	10.5	15.75	28.75	3.11	
21.	I	0.99	14.20	9.73	9.88	4.49	4.53	2.49	13.68	0.99	1.50	2.74	0.21	1:5
22.	II	0.99	14.20	9.48	9.62	3.99	4.03	4.74	26.04	0.99	1.50	1.5	0.11	Fly ash:
23.	III	2.0	28.69	31.4	31.88	2.0	2.02	2.99	16.43	2.99	4.54	810.5	60.96	sludge
24.	IV	0.99	14.20	39.9	40.51	80.8	81.61	2.99	16.43	53.9	81.84	384.0	28.88	
25.	V	2.0	28.69	7.98	8.10	7.73	7.81	4.99	27.42	6.99	10.61	130.8	9.78	

It should be remembered that metals bound with manganese and iron oxides as well as with the organic substance are still a potential source of metals available to plants, however their immobilization progresses much slower.

In the residual determined as fraction V, lead and nickel were bound in the highest percentage, then cadmium, chromium, copper and zinc. Metals bound in fraction V are totally unavailable to the environment.

In the analyzed wastewater sludge, main role in copper and chromium accumulation plays fraction IV – organic; while for nickel, zinc and cadmium – fraction III – iron and manganese oxides and in the case of lead – fraction V – residuals. Analysis of data from bottom sediments and soil speciation obtained by J. Siepak [9] shows similarity in metals behaviour.

Due to the lack of data on the speciation of sludge-ash composite, a comparative analysis with the data obtained in course of own research is impossible.

CONCLUSIONS

1. Sanitation of wastewater sludge originating from a municipal wastewater treatment plant with fly ash from dry desulphurisation of flue gas from a power plant is feasible. The performed investigation showed that regardless of the proportion of sludge to fly ash (1:1, 1:2, 1:4, 1:5) positive bacteriological effects were observed already after three days. It is difficult to discuss sanitation in terms of parasites as they did not occur also in sludge after dehydration.

2. The content of heavy metals introduced to sludge along with the fly ash was comparable to the metal content in sludge, except for nickel whose significantly higher amount was identified in ash as well as zinc and lead whose content was higher in sludge.

3. Addition of wastewater sludge and fly ash mixture (in one of the analyzed mixtures) to soils shall not result in an increased risk posed by heavy metals.

4. Metal bonds in sludge and ash mixtures are similar to bonds observed in pure wastewater sludge. After speciation analysis it should be stated that such heavy metals as lead, chromium, nickel, cadmium and zinc pose most serious risk to soils, water and plants. They are mainly bound in poorly soluble fractions (fractions III – V), thus poorly available to the ecosystem.

5. Primarily due to economic reasons, to achieve sludge sanitation effect, it is sufficient to apply 1 weight portion of fly ash per 5 weight portions of wastewater sludge.

6. Speciation analysis of metals, as an analysis of future also in wastewater sludge management technologies, allows for a detailed discussion, frequently correlating with other factors, as well as for a correct determination of the level of threat posed to the natural environment.

REFERENCES

[1] Biernacka J., J. Sałbut, M. Kazimierczuk: *Tlenowo-beztlenowa stabilizacja osadów ściekowych wraz z ich higienizacją (Aerobic-anaerobic stabilisation of wastewater sludge and its sanitation)*, IOŚ, maszynopis (typewrite), Warszawa 1990.

[2] Marcinkowski T.: *Procesy stabilizacji osadów a efektywność niszczenia organizmów patogennych (Sludge stabilisation processes and effectiveness of pathogenic organisms destruction)*, [w:] Materiały Krajowej Konferencji Naukowo-Technicznej nt. Wykorzystanie osadów ściekowych – techniczne i prawne uwarunkowania, Częstochowa 1996, 29 – 34.

[3] Piotrowska M., S. Dutka: *Frakcje metali śladowych w osadach ściekowych jako kryterium ich przydatności w rolnictwie (Trace metals fractions is wastewater sludge as criterion of its applicability for agricultural purposes)*, Arch. Ochr. Środ., 1 – 2, 65 – 72 (1987).

[4] Rosik-Dulewska C.: *Ocena ilościowa i jakościowa metali ciężkich w osadach ściekowych w aspekcie ich przyrodniczego wykorzystania (Qualitative and quantitative analysis of heavy metals in wastewater sludge in the aspect of its natural use)*, [w:] Materiały Konferencji Naukowej nt. Bioremediacja gruntów, Gliwice – Wisła 1998, 213 – 222.

[5] Rosik-Dulewska C., M. Miksztа: Dynamika ługowania metali ciężkich z gleb nawożonych osadami ściekowymi (Dynamics of heavy metals leaching from soils fertilized with wastewater sludge), [w:] Materiały III Konferencji Naukowo-Technicznej nt. Przyrodnicze użytkowanie osadów ściekowych, Świnoujście 1999, 151–160.

[6] Rosik-Dulewska C.: *Przydatność osadów ściekowych do przyrodniczego zagospodarowania w świetle jakościowej oceny metali ciężkich (Applicability of wastewater sludge for natural use in the light of qualitative assessment of heavy metals)*, [w:] Materiały Konferencyjne nt. Postęp techniczny w dziedzinie oczyszczania ścieków, Katowice 1999, 38–50.

[7] Rosik-Dulewska C.: *Podstawy gospodarki odpadami (Principles of waste management)*, Ekoinżynieria, Lublin 1999.

[8] Sawa J.: *Modyfikacja osadów ściekowych w Oczyszczalni Ścieków "Hajdów" w Lublinie (Modification of wastewater sludge in "Hajdów" Wastewater Treatment Plant in Lublin)*, [w:] Materiały III Konferencji Naukowo-Technicznej nt. Przyrodnicze użytkowanie osadów ściekowych, Świnoujście 1999, 143–150.

[9] Siepak J. [red].: *Analiza specjacyjna metali w próbkach wód i osadów dennych*, Poznań UAM 1998.

[10] Siuta J. [red].: *Przyrodnicze zagospodarowanie osadów ściekowych (Natural utilization of wastewater sludge)*, PWN, Warszawa 1988.

[11] Siuta J. [red.].: *Przyrodnicze użytkowanie osadów ściekowych (Natural Use of wastewater sludge)*, Materiały konferencyjne, Ekoinżynieria, Lublin, 1996.

[12] Siuta J.: *Rekultywacyjne użytkowanie osadów ściekowych (Application of wastewater sludge for reclamation purposes)*, [w:] Krajowa Konferencja Naukowo-Techniczna nt. Wykorzystanie osadów ściekowych – techniczne i prawne uwarunkowania, Częstochowa 1996, 85–92.

[13] Tessier A., M. Bisson, P.B.C. Campbell: *Sequential Extraction Procedure for the Speciation of Particulate Trace Metals*, Analytical Chemistry, **51**, 7, 844–851 (1979).

[14] Wytyczne IOŚ *(Guidelines of the Institute of Environmental protection), Przyrodniczo-techniczne przetwarzanie osadów ściekowych na kompost*, Ministerstwo Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa – IOŚ, Warszawa 1995.

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