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Influence of Old Landfill Leachate Co-digestion with Sewage Sludge on Heavy Metals Concentration in Digester Effluent

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1. Introduction

The concept of sustainable development formulated by the Brundtland (1986) gave rise to a more holistic treatment of environmental related problems. Today, sustainable development belongs to one of the most important principles, which sets out the theoretical concepts in the functioning of the contemporary world, although the practical implementation of sustainable development is not simple goal [13, 14]. In subsequent years the idea of sustainable development was further developed and refined. As a result, it became multi-dimensional, with recommendations for implementing sustainable development, initially focusing on the protection of the environment, but quickly is covering other areas of human activity starting with the management of Earth's resources and ending with the ethical aspects. Consequently, the transformation of the functioning of civilisation, in accordance with the sustainable development paradygms, have become recognised as the beginning of a new revolution in the development of civilisation [2]. An important issue on which depends the survival of human civilization is to ensure the energy supply. In recent years, great importance is attached to the use of waste for energy production. One of the way leading to energy recovery form waste is anaerobic digestion. The one of the most suitable material for this process is sewage sludge from municipal wastewater treatment plant.

The disposal of sludge is a problem of growing importance, representing up to 50% of the current operating costs of a wastewater treatment plant (WWTP). It is possible to utilize it in anaerobic digestion process [12, 13]. Anaerobic treatment of sewage sludge leads both to sludge volume reduction and its stabilization and to biogas production. However, operational data have indicated possible reserves of the digesters' capacity, frequently as much as 30%, so it is possible to introducing additional components to the co-digestion process. The co-digestion process, also called the co-fermentation or biomethanization of selected waste mixture. Some wastes like sewage sludge, source-sorted organic fraction of municipal solid waste, manure, farm waste and some industrial organic wastes (e.g. food waste) are suitable for co-digestion. Such co-substrates could effectively be degraded under specific environmental conditions (pH, temperature, hydrogen concentration). However, some co-substrates require a comprehensive and costly pretreatment (e.g. source-separated organic fraction from municipal waste or lignocellulose-based waste); some, due to their potential hygienic risk, have to be treated by thermal hygienization [10]. Benefits of co-digestion consist in:

- dilution of toxic substances coming from any of the substrates involved,
- improved nutrient balance,
- higher biogas yield and an increased load of biodegradable organic matter,
- synergetic effects on microorganisms,
- high digestion rate,
- possible removal of some xenobiotic organic compounds.

Landfilling is still widely used for waste disposal mainly due to cheap exploitation and low capital cost. Landfills can be treated as an anaerobic bioreactors which allow to biogas recovery [11]. However anaerobic degradation of solid waste results in leachate production. Landfill leachate is generated by excess rainwater percolating through the waste layer as a mixture of high concentrated organic and inorganic contaminants that include humic acids, ammonia nitrogen, heavy metal and xenobiotics. The substances in question need to be removed due to their toxicity and negative effect on the environment. Landfill leachate treatment is very difficult both from economic and environmental point of

view. A knowledge concerning leachate composition and variation of its flow rate is critical for choosing a suitable treatment strategy. Generally, leachate treatment requires various, frequently combined biological and/or physicochemical methods. Using landfill leachate as a co-substrate to the co-digestion process seems to be a promising solution due to a high concentration of leachate contaminants, particularly soluble organic matter (expressed as soluble COD, TOC and VFA). Among many technological approaches to leachate treatment, co-digestion of leachate and sewage sludge seems to be worth considering [6, 7]. Heavy metals are present in sewage sludge in significant concentrations. It is commonly known that these metals are not biodegradable and can accumulate to potentially toxic levels. Moreover, they can affect the sewage sludge degradation efficiency and microbes growth. It was found that toxicity of heavy metals is one of the main causes of failure of the process or digester upset [3, 4, 9]. It is generally believed that acidogens are more resistant to the toxic influence of heavy metals than methanogens. The toxic effect is attributed to disruption of enzyme function and structure by binding of the metals with thiol and other groups on protein molecules or by replacing naturally occuring metals in enzyme prosthetic groups [15]. On the other hand, many of heavy metals are required as a part of the essential enzymes that drive numerous anaerobic digestion reactions. According to Alvarez et al. [1] higher concentrations of heavy metals were presented in the primary sludge than in secondary one. Sequential extraction of Al, Cr, Fe and Pb concentrations indicated a significant increase in the residual fraction after anaerobic digestion. The oxidizable Cd and Zn fraction also increased after digestion. The conversion of heavy metals during anaerobic digestion results from decay of the organic matter associated with metal, either due to formation of insoluble metal sulfides (Fe, Pb) or by transformation (reduction) in the case of Cd and Ni. Karvelas et al. [8] investigated the occurrence and partition of heavy metals (Cd, Pb, Mn, Cu, Zn, Fe and Ni) in the activated sludge. Ni and Mn were found mainly in soluble phase (80–93% and 65–85% respectively), while Cu, Cr, Pb, Cd and Zn were mostly associated with the particulate phase (65–95%). Also, Fe formed association with particles (58–75%). Czekala et al. [5] investigated heavy metal concentrations in sewage sludge from eight different wastewater treatment plants. The concentration of analyzed heavy metals in each particular fraction is different in each of WWTPs. In general, the total content of Cd, Cu, Zn, Cr and Ni in the two most labile fraction did not exceed 2.9%. However, the

environmental impact analysis of digest should also be undertaken. In the present study variability of heavy metal concentrations in the co-digestion process of sewage sludge and old landfill leachate was examined.

2. Materials and methods

2.1. Material characteristics and sample preparation procedure

Sludge used as material for the study was obtained from Puławy municipal wastewater treatment plant (WWTP), Poland, as primary thickened sludge and waste thickened sludge. Leachate was achieved from Rokitno municipal solid waste landfill of old age (landfill age more than 10 years old). Sludge was sampled once a week in Puławy WWTP and then provided immediately to the laboratory of the Lublin University of Technology. Primary and waste sludge were transported in separate containers. Under laboratory conditions, sludge was mixed at volume ratio of 60:40 (primary:waste sludge), then homogenized, manually screened through a 3 mm screen and partitioned The sludge samples were frozen at -25°C in laboratory freezer and thawed daily for 12 h at 20°C in the indoor air. Sludge prepared in this manner fed the reactor as mixed sludge. The general characteristics of sludge are shown in Table 1.

Table 1. Characteristics of mixed sewage sludge
Tabela 1. Charakterystyka mieszaniny osadów ściekowych

Parameter	Unit	Average value	Upper/Lower 95% mean
COD	mg L^{-1}	42519	45611/39427
TOC (*)	mg L^{-1}	720	854/586
VFA	mg L^{-1}	1710	2188/1232
TS	g kg^{-1}	39.0	42.3/35.7
VS	g kg^{-1}	28.7	30.1/27.3
pH	–	6.36	6.44/6.28
Alkalinity	mg L^{-1}	956	982/930
$N\text{-}NH_4^+$	mg L^{-1}	150.8	210.5/91.1
$P\text{-}PO_4^{3-}$	mg L^{-1}	176.2	217.0/135.4

Leachate was sampled once as averaged collected sample taken from leachate storage tank, and transported, as soon as possible, to the

laboratory. Then it was homogenized, partitioned, frozen and storage at -25°C in a laboratory freezer. The leachate samples were thawed daily for 6 h at 20°C. Leachate composition is presented in Table 2.

Table 2. Leachate composition – average values
Tabela 2. Skład odcieku – wartości średnie

Parameter	Unit	Average value
COD	mg L^{-1}	6615
BOD_5	mg L^{-1}	355
BOD_5/COD	–	0.05
TOC	mg L^{-1}	2495
pH	–	8.12
Alkalinity	mg L^{-1}	15050
VFA	mg L^{-1}	426
TS	g kg^{-1}	12.05
VS	g kg^{-1}	2.24
N_{NH4+}	mg L^{-1}	1390
P_{PO4}^{3-}	mg L^{-1}	6.2

2.2. Laboratory installation

The laboratory installation constitutes anaerobic, a completely mixed reactor (with a working volume of 40 dm^3) equipped with gaseous installation, an influent peristaltic pump and storage vessels. Mixing was carried out using a mechanical stirrer. Influent was supplied to the upper part of digester, effluent was wasted through the bottom by gravity. The gas system consisted of pipelines linked with the pressure equalization unit, the drum gas meter and gas sampler with a rubber septum. The laboratory installation is shown in Figure 1.

2.3. Operational set-up

An inoculum for the laboratory reactor was taken from Puławy wastewater treatment plant as a collected digest from a mesophilic anaerobic digester. The adaptation of the digester biomass was achieved after 30 days. The study was carried out in the temperature of 35°C and in semi-flow mode (digester was supplied regularly once a day). Three runs were conducted and each experiment was continued over 60 days.

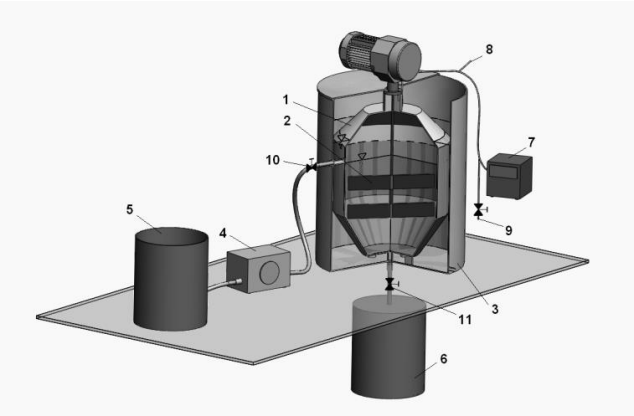

Fig. 1. Laboratory installation for co-digestion process; 1 – anaerobic reactor, 2 – mechanical stirrer, 3 – heating jacket, 4 – influent peristaltic pump, 5 – influent storage vessel, 6 – effluent storage vessel, 7 – drum gas meter, 8 – gaseous installation and gas sampler with a rubber septum, 9 – dewatering valve, 10 – inlet valve, 11 – outlet valve
Rys. 1. Stanowisko badawcze do procesu współfermentacji; 1 – reaktor beztlenowy, 2 – mieszadło mechaniczne, 3 – płaszcz grzewczy, 4 – dozująca pompa perystaltyczna, 5 – zbiornik z nadawą, 6 – zbiornik z odpływem, 7 – gazomierz bębnowy, 8 – instalacja gazowa i próbnik gazu z gumową przegrodą, 9 – zawór odwadniający, 10 – zawór wlotowy, 11 – zawór wylotowy

In the first run (R1) the reactor was fed daily with 2 L of mixed sludge. Hydraulic retention time (HRT) reached 20 days and hydraulic loading rate was 0.05 d^{-1}. Organic loading rate (OLR) was time-dependent and ranged from 1.50 to 1.55 kg VS $m^{-3}d^{-1}$. During second run (R2) reactor was fed with 2.1 L using sludge with leachate addition in a volumetric ratio of 20:1. HRT reached 19 days and hydraulic loading rate was 0.053 d^{-1}. OLR ranged from 1.38 to 1.48 kg VS $m^{-3}d^{-1}$. In the third run (R3) arrangement was the same as in R2, but a volumetric ratio of sludge and leachate was assumed at 10:1, thus feed was 2.2 L. HRT reached 18 days and hydraulic loading rate was 0.055 d^{-1}. OLR ranged from 1.61 to 1.69 kg VS $m^{-3}d^{-1}$.

2.4. Analytical methods

Analysis of total metal content in sludge and leachate was carried out using ICP-OES method (optical emission spectrometry). Quantitative

analysis was performed on a JY238 Ultrace (Jobin Yvon-Horriba, France) using direct calibration method after microwave digestion. The samples of homogenized sludge (1 g) were digested in acid mixture of HNO_3:HCl (5:2), while digestion of leachate samples (15 g) required only HNO_3 addition (3 ml). The digestion process lasted 45 min. at 180°C and the pressure of 18 bars. Metal concentrations were determined at different emission bands presented in Table 3. Detection limits were established individually for each measurement series and they did not exceed 10 ppb units for most metals.

Table 3. Wave-lengths used in metal determination
Tabela 3. Długości fal wykorzystane do analizy zawartości metali w próbkach

Metal	Wave-length	Metal	Wave-length
Al	308.215	Fe	259.940
	394.401	Mn	257.610
Cd	228.802	Mo	202.030
Co	228.616	Ni	221.647
Cr	267.716	Pb	220.353
Cu	324.754	Zn	213.856

3. Results and discussion

A determination of average metal concentrations both in mixed sewage sludge and in old landfill leachate were performed. The results are presented in Table 4. Moreover, an observation of the changes of metal concentration before and after digestion was carried out to evaluate the environmental impact analysis of digested medium. Table 5 shows the average metal concentrations in digester influent and effluent during experiments.

The results indicated that metal concentrations in leachate were much lower than the values measured in the mixed sludge. Taking into consideration that leachate doses reached only 5% and 10% in comparison to the volume of mixed sludge, their influence on the metal concentrations in the influent stream was negligible in most cases. It was just assumed that an addition of old landfill leachate probably diluted sewage sludge, thus the metal concentrations in feed decreased in most cases. In contrast, the opposite tendency appeared on the dry weight basis

(Table 7). An increase of the total metal content in R2 and R3 feed occurred due to the lower TS content (Table 6). The relative abundance of metals in sewage sludge samples before digestion followed the general order: Cd < Co < Mo < Ni < Pb< Cr < Cu < Mn < Zn < Fe <Al (Table 5). An analogous sequence was achieved for samples enriched by old landfill leachate (only Mo and Co, Cd changed position between each other in R2 and R3). These results are consistent with research by other authors [3] focused on sewage sludge, although in those studies a minor group of metals was investigated and their concentrations were one order of magnitude higher (excepting Cd and Pb). This could be explained by the lack of high industrial loads supplying the Puławy WWTP, which was reflected in metal-weak composition of sewage sludge.

Table 4. Average metal concentrations in co-digested components (mg L^{-1})
Tabela 4. Stężenia metali ciężkich w substratach poddawanych współfermentacji (mg L^{-1})

Metal	Mixed sewage sludge	Rokitno leachate
Al	189.2519	2.5645
Cd	0.02945	0.0000
Co	0.0643	0.0832
Cr	0.6153	0.8554
Cu	3.3770	1.1765
Fe	165.9537	4.0918
Mn	8.5690	0.2358
Mo	0.1087	0.0261
Ni	0.2918	0.3882
Pb	0.5506	0.0421
Zn	22.2478	1.6141

The concentrations of most the metals measured in the effluent increased in comparison to influent data. The differences between levels before and after digestion of sewage sludge (R1) reached minimum 22% for Al and maximum for Cd (concentration of Cd in effluent was 2.5 times higher than in the mixture of sludge feeding the reactor). The increases of the concentration of others metals as Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were as follows: 33%, 42%, 57%, 36%, 35%, 68%, 38% and 45%. This observation is compatible with the research by Chipasa [3].

The author found that Cd,Cu, Pb and Zn concentrations in digested sludge exceeded the corresponding values in undigested sludge by 50–99%. The metal concentrations observed in the effluents were comparable for all runs, thus the addition of leachate was not found as a determinant of the co-digestion effluent quality.To evaluate the "real" effect of old landfill leachate addition on digest quality, calculation of the average loads of specified metals (expressed in mg kg^{-1} TS) was conducted for both their influents and effluents (Table 7).

Table 5. Average metal concentrations in digester influent and effluent during experiments (mg L^{-1})
Tabela 5. Średnie wartości stężeń metali na dopływie i odpływie z reaktora podczas eksperymentu (mg L^{-1})

Metal	R1		R2		R3	
	influent	effluent	influent	effluent	influent	effluent
Al	157.25	191.87	172.82	249.33	134.68	173.51
Cd	0.02	0.05	0.13	0.13	0.06	0.39
Co	0.09	0.12	0.004	0.00	0.04	0.07
Cr	0.65	0.92	1.20	1.12	0.42	0.63
Cu	3.35	5.28	4.50	6.69	4.05	4.84
Fe	145.43	198.22	204.02	269.19	132.57	179.61
Mn	8.33	11.22	8.93	11.029	6.93	8.67
Mo	0.08	0.016	0.18	0.229	0.14	0.22
Ni	0.31	0.52	1.03	0.779	0.39	0.46
Pb	0.48	0.66	0.80	1.35	0.78	0.77
Zn	21.43	31.08	24.69	37.17	22.58	26.36

Table 6. Total solids (TS) concentration during runs
Tabela 6. Stężenie suchej masy organicznej w dopływie i w odpływie z reaktora

Parameter	Unit	R1		R2		R3	
		feed	digest	feed	digest	feed	digest
TS	g kg^{-1}	30.5	17.5	27.2	16.0	30.0	16.0

Quantitative analysis and comparison of the results showed an almost twofold increase in the effluent loads of most metals as compared to their levels in the influent during R1 (the increase ratio ranged from 0.2 to 2.5 for the various metals). During R2, the increase ratios oscillated around the value of 1.14. In R3, the evaluated ratios varied over a wider range. However, in most cases their values were lower than in the R1 and R2 experiment (except for copper). The final metal concentrations of the dry sludge showed a general decrease in the levels of the specified metals as a result of co-digestion. Such an observation is consistent with the results provided by Hombach et al. [7]. It might indicate that in co-digestion systems microorganisms were able to generate specific substances allowing for selective uptake of metals. However, further studies involving metal speciation would have to be undertaken. In principle, the content of metals after anaerobic digestion of sewage sludge and old landfill leachate was in accordance with the compliance limits for agriculture land application (issued by directive 86/278/EWG).

It can be assumed that the leachate additions did not have a negative effect on the anaerobic digestion of the sewage sludge.

Table 7. Average total metal content on dry weight basis (mg kg TS^{-1})
Tabela 7. Średnie stężenia metali w przeliczeniu na suchą masę organiczną (mg kg TS^{-1})

Metal	R1		R2		R3	
	feed	digest	feed	digest	feed	digest
Al	5156	10964	6354	15583	4489	7922
Cd	0.7	2.9	4.8	8.1	2.0	3.5
Co	3.0	6.9	0.1	0.0	1.3	2.4
Cr	21.3	52.6	44.1	70	14	24.7
Cu	109.8	301.7	165.4	418.1	135	238.2
Fe	4768	11327	7501	16824	4419	7798
Mn	273.1	641.1	328.3	689.3	231	407.6
Mo	2.6	0.9	6.6	14.3	4.7	8.2
Ni	10.2	29.7	37.9	48.7	13	22.9
Pb	15.7	37.7	29.4	84.4	26	45.9
Zn	702.6	1776	907.7	2323	752.7	1328

4. Conclusions

The results indicated that leachate produced in old landfill (over 10 years), co-digested with sewage sludge from municipal wastewater treatment plant did not significantly influence the concentration of heavy metals in bioreactor effluent. The concentration of examined metals in leachate were much lower than the values observed in the mixed sludge. The metal concentrations observed in the digests were comparable for all the experimental runs. Thus the addition of leachate was not found as a determinant of the co-digestion effluent quality. This seems to indicate that co-fermentation of sewage sludge and landfill leachate could be considered as a harmless method of old leachate utilization.

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Wpływ współfermentacji starych odcieków z osadami ściekowymi na stężenia metali ciężkich w osadzie przefermentowanym

Streszczenie

Przedmiotem badań była analiza wpływu zanieczyszczeń pochodzących z odcieków pozyskiwanych ze składowisk odpadów komunalnych wieku powyżej 10 lat dodawanych jako kosubstrat do procesu biometanizacji mieszanych osadów ściekowych na stężenia metali ciężkich w osadzie przefermentowanym. Eksperyment obejmował badania modelowe fermentacji mezofilowej (w temperaturze 35°C) osadów pochodzących z systemu gospodarki osadowej miejskiej oczyszczalni ścieków w Puławach, mieszanych objętościowo w odpowiednich proporcjach z odciekami pochodzącym ze starej niecki składowiska odpadów

komunalnych w Rokitnie. Osad poddawany fermentacji w reaktorze kontrolnym stanowił mieszaninę zagęszczonego grawitacyjnie osadu wstępnego oraz zagęszczonego mechanicznie osadu nadmiernego, przy czym udziały objętościowe poszczególnych osadów wynosiły odpowiednio 60:40.

Badania prowadzono w trzech etapach, z zastosowaniem dwóch różnych dawek odcieku. Stężenia metali określano w mieszaninie zasilającej reaktor oraz w osadzie przefermentowanym. Badano stężenia następujących metali: Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn. W celu określenia wpływu środowiskowego osadów przefermentowanych określano zmienność ich stężeń przed i po procesie współfermentacji. Otrzymane wyniki wskazują, że stężenia metali w odcieku były niższe niż w mieszaninie osadów. Stężenia metali na odpływie z reaktora były na porównywalnym poziomie podczas wszystkich etapów eksperymentu, może to wskazywać że dodatek odcieków nie powodował pogorszenia jakości osadu przefermentowanego. Współfermentacja odcieków pochodzących ze starych składowisk i osadów ściekowych wydaje się być odpowiednią metodą ich utylizacji.