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Co-digestion of Sewage Sludge and Organic Fraction of Municipal Solid Waste in the Aspect of Heavy Metals Content

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1. Introduction

The disposal of sludge is a problem of growing importance. Municipal WWTPs produce sludge as a by-product of the physical, chemical and biological wastewater treatment processes. One of possible method of its utilization is an anaerobic digestion process (AD). The AD process provides the degradation and stabilization of organic matter under anaerobic conditions in the presence of microbial organisms. It leads to the generation of biogas and microbial biomass, also a stabilized product (digest) is obtained.

Heavy metals are present in sewage sludge in significant concentrations. Their concentrations are a vital parameter in methane formation during the anaerobic digestion. Trace elements like copper, zinc, soluble forms of magnesium, potassium and calcium are essential for microbial growth in the digester. Some microorganisms can also remove toxic metals from feedstock. It is commonly known that these metals are not biodegradable and can accumulate to potentially toxic levels. Metal concentration cannot exceed the acceptable standards and they should also be monitored before anaerobic digestion. Toxic metals such as cadmium and lead can inhibit biogas/methane production and process efficiency (Bożym et al. 2015). Typical metal content in sludge is about 0.5-2% on the dry weight basis and may even go up to 4%. It depends on many factors, such as the local conditions (mainly the type of industries), wastewater quality,

environmental factors, or the sludge treatment method used (Chipasa 2003, Chen et al. 2008, Czechowska-Kosacka et al. 2015).

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 (Mudhoo and Kumar 2013). 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 occurring metals in enzyme prosthetic groups (Yue at al. 2007). On the other hand, many heavy metals are required as a part of the essential enzymes that drive numerous anaerobic digestion reactions. According to Alvarez et al. (2002), higher concentrations of heavy metals were present 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 the formation of insoluble metal sulfides (Fe, Pb) or by transformation (reduction) in the case of Cd and Ni. Karvelas et al. (2003) 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 the soluble phase (80-93% and 65-85% respectively), while Cu, Cr, Pb, Cd and Zn were mostly associated with the particulate phase (65-95%). Fe also exhibited association with particles (58-75%). The heavy metals concentration in sewage sludge from eight different wastewater treatment plants was investigated by Czekala et al. (2002). In general, the total content of Cd, Cu, Zn, Cr and Ni in the two most labile fraction did not exceed 2.9%. The aim of the study of Abdel-Shafy and Monsur (2014) was to investigate the effect of selected heavy metals on biogas production from sewage sludge. The general ranking of heavy metals toxicity was Hg > Cd > Cr (III). The research revealed that heavy metals addition to feedstock caused a decrease of biogas production and reduction of the process efficiency. Decomposition of organic substances via anaerobic digestion, results in an increase of heavy metal concentration in the dry matter of stabilized sewage sludge. However, besides the determination of the total heavy metal con-

centration in stabilized sludge, it is crucial to determine the chemical forms in which heavy metals occur, since these forms determine their mobility and bioavailability.

Anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) has been widely implemented in recent years. The main factors underlying this increase include: (i) legislation limiting landfill treatment of biodegradable waste (99/31/EC), (ii) increase of waste sorted in source, and (iii) anaerobic treatment of biodegradable fraction resulting in enhanced energy production. According to these favorable circumstances, co-digestion of organic fraction of municipal solid waste has become an active area of research due to its potential advantages compared to conventional anaerobic digestion. The literature contains a number of reports on successful digestion of OFMSW co-digested with primary and/or excess activated sludge (Krupp et al. 2005; Sosnowski et al. 2003, Zupančič et al. 2008, Grassmug et al. 2003); livestock wastes (Hartmann and Ahring 2005). However, the subject area has not been studied in the aspect of heavy metals.

2. Materials and methods

2.1. Material characteristics

Sewage sludge that included two-source residues was obtained from the Puławy municipal wastewater treatment plant (WWTP), Poland, using primary and secondary treatments. Sludge was sampled once a week in the WWTP. Primary sludge from gravity thickener and waste sludge from mechanical belt thickener were transported in separate containers. Under laboratory conditions, sludge was mixed at the volume ratio of 60:40 (primary:waste sludge), then homogenized, manually screened through a 3 mm screen and partitioned. The sludge samples were stored at 4°C in a laboratory fridge for a week at most. Sludge prepared in this manner (signed as SS) was used as material for the study. The organic fraction of municipal solid waste was obtained from waste treatment plant in Puławy. The waste treatment plant collect recyclable waste and mixed municipal solid waste. Mixed municipal solid waste undergo hydromechanical processing according to BTA technology (Biotechnische Abfallverwertung, Germany) consisting of mechanical separation, removal of metals using magnetic separator and pulping using landfill leachate to

achieve the dry mass content on the level of 4-6%. The OFMSW was sampled from the storage tank, once for the whole experimental period. The OFMSW samples were prepared in the same manner as the sewage sludge (without screening). The main characteristics of SS and OFMSW during experiments are presented in Table 1. Moreover, the average metal content in both substrates are given in Table 2.

Table 1. Characteristics of substrates (average values are given)
Tabela 1. Charakterystyka substratów (wartości średnie)

Parameter	Unit	SS	OFMSW
COD	mg L^{-1}	44518	16511
pH	-	6,58	6.08
CODs	mg L^{-1}	-	9250
Alkalinity	mg L^{-1}	852	4050
Volatile Fatty Acids (VFA)	mg L^{-1}	1236	5099
Total Solids (TS)	g kg^{-1}	38.3	18.2
Volatile Solids (VS)	g kg^{-1}	29.3	11.1
N_{NH4+}	mg L^{-1}	109.1	297
P_{PO4}^{3-}	mg L^{-1}	139.1	26.5

Table 2. Average heavy metals concentration in substrates
Tabela 2. Średnie stężenia metali ciężkich w substratach

Metal	Average values of heavy metal concentrations, mg L^{-1}	
	SS	OFMSW
Al	189.25	117.38
Cd	0.03	nd.
Co	0.064	nd.
Cr	0.615	3.791
Cu	3.377	0.803
Fe	165.95	68.73
Mn	8.569	3.990
Mo	0.109	0.052
Ni	0.292	nd.
Pb	0.551	nd.
Zn	22.25	6.16

nd. – not detected

2.2. Laboratory installation and operational set-up

The study was performed in anaerobic reactors operating at the temperature of 35°C in semi-flow mode (digester was supplied regularly once a day). The laboratory installation consisted of two completely mixed digesters (with an active volume of 40 dm^3) working in parallel, equipped with a gaseous installation, an influent peristaltic pump and storage vessels (Fig. 1).

Feed was supplied to the upper part of the digester, digest was wasted through the bottom by gravity. The gas was taken up using a system consisting of pipelines linked with the pressure equalization unit and a mass flow meter.

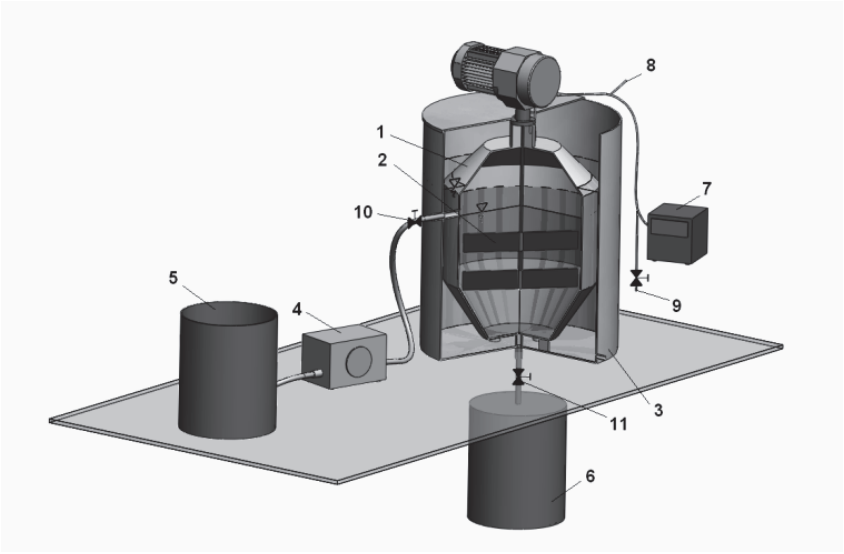

Fig. 1. Laboratory installation for co-digestion process
1 – anaerobic reactor, 2 – mechanical stirrer, 3 – heating jacket, 4 – influent peristaltic pump, 5 – influent storage vessel, 6 – effluent storage vessel, 7 – drum gas meter, 8 – gaseous installation and gas sampler with a rubber septum, 9 – dewatering valve, 10 – inlet valve, 11 – outlet valve
Rys. 1. Stanowisko badawcze do procesu współfermentacji

An inoculum for the laboratory reactors was taken from Puławy wastewater treatment plant as a collected digest from a mesophilic anaerobic digester operating at 35-37°C with the volume of 2500 m^3, organic loading rate (OLR) of 0.5 kg VS m^{-3} d^{-1} and hydraulic retention time

(HRT) of about 25 days. The adaptation of the digester biomass was achieved after 30 days.

Two reactors (R1, R2) were used and two experimental phases were conducted. Reactor R1 was fed with 100% SS (1.R1 and 2.R1) in both phases, whilst reactor R2 was fed with mixtures of SS and OFMSW: 75:25 and 70:30 by volume, respectively, in the first phase (1.R2) and in the second one (2.R2). The feed composition and operational parameters are presented in Table 3.

Table 3. Feed composition and operating regime during experiments
Tabela 3. Skład wsadu oraz warunki operacyjne procesu

Run	Feed composition	Feed volume dm^3	HRT d	OLR kg VS $m^{-3}d^{-1}$
1.R1	SS	2.0	20	1.37
1.R2	SS+OFMSW 75:25 v/v	2.0 (1.5 + 0.5)	20	1.17
2.R1	SS	2.0	20	1.37
2.R2	SS+OFMSW 70:30 v/v	2.0 (1.5 + 0.6)	20	1.08

2.4. Analytical methods

Determination of total metal content both in the feed that supplied the reactors and in the digest released from them 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 homogenized samples of 1g were digested in acid mixture of HNO3:HCl (5:2). The digestion process lasted 45 minutes at 180°C and the pressure of 18 bars.

The concentrations of the following metals were determined: Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn. This was made at different emission bands and specified wave lengths (Table 4). Detection limits were established individually for each measurement series and did not exceed 10 ppb units for most metals.

Table 4. Wave-lengths and limits of detection (ppb) used in metal determination using ICP-OES (nm)
Tabela 4. Długości fal oraz limity detekcji (ppb) wykorzystane do analizy zawartości metali w próbkach (nm)

Metal	Wave-length	LOD ppb	Metal	Wave-length	LOD ppb
Al	308.215	9.71	Fe	259.940	0.92
	394.401	9.90	Mn	257.610	4.02
Cd	228.802	0.24	Mo	202.030	0.92
Co	228.616	0.62	Ni	221.647	0.40
Cr	267.716	0.39	Pb	220.353	0.38
Cu	324.754	2.02	Zn	213.856	6.77

3. Results and discussion

To evaluate the environmental impact analysis of the digested medium, an observation of the changes of total solids, volatile solids and metal concentrations before and after digestion was carried out for anaerobic digestion and co-digestion systems. The average values of TS and η_{VS} achieved during experiments are given in Table 5.

Table 5. Total solids (TS) and volatile solids removal (η_{VS}) during runs
Tabela 5. Sucha masa i stopień przefermentowania (η_{VS})

Parameter	Unit	1.R1		1.R2		2.R1		2.R2	
		feed	digest	feed	digest	feed	digest	Feed	digest
TS	g kg^{-1}	36.6	25.2	32.0	23.4	36.8	25.1	29.9	20.9
η_{VS}	%	39.1		39.8		41.1		42.8	

The results indicated that co-digestion of sewage sludge and OF-MSW was more efficient (1.R2 and 2.R2) as compared to the control runs (1.R1and 2.R1). Total solids were found to be decreased along with a dose of OFMSW in feed and digest (due to dilution of the reactor influ-

ent and an effective decomposition of substrate). Moreover, volatile solids removal was higher after addition of OFMSW.

Determination of an average total metal content on dry weight basis was evaluated for environmental impact analysis (Table 6).

Table 6. Average total metal content on dry weight basis, mg kg TS^{-1}
Tabela 6. Średnie stężenie metali ciężkich w przeliczeniu na suchą masę, mg kg TS^{-1}

Metal	1.R1		1.R2		2.R1		2.R2	
	feed	digest	feed	digest	Feed	digest	Feed	Digest
Al	5975.96	10635.69	6043.44	13911.97	5491.30	10385.66	5908.70	8737.80
Cd	1.09	2.75	0.94	1.71	0.82	2.39	0.67	1.91
Co	1.64	3.14	1.56	4.70	1.90	3.59	1.67	4.78
Cr	18.31	40.39	45.31	70.51	17.66	41.04	53.18	78.47
Cu	102.19	208.24	94.06	219.66	83.70	178.88	80.27	262.68
Fe	5585.52	11063.14	5328.44	13796.15	4358.70	9300.80	4678.93	8436.84
Mn	233.88	473.33	231.88	546.15	257.61	543.82	261.87	531.10
Mo	3.01	6.27	3.13	10.26	3.53	7.97	3.68	8.61
Ni	9.02	18.82	7.81	28.21	6.25	13.15	5.35	35.89
Pb	15.85	34.51	13.75	54.70	20.11	43.43	17.39	43.06
Zn	682.51	1361.57	633.75	1469.66	558.42	1162.55	542.81	1111.48

The relative abundance of metals in sewage sludge samples before anaerobic digestion followed the general order: Cd < Co < Mo < Ni < Pb < Cr < Cu < Mn < Zn < Fe <Al (only Cr and Pb swapped their positions in 2.R1). An analogous sequence was reached after the addition an OFMSW as a co-substrate. These results are consistent with the study by other authors (Obarska-Pempkowiak and Gajewska 2008) focused on sewage sludge. However, Dong et al., (2013) noted a different order: Pb < Ni < Cu < Cr < Zn for sewage sludge during high-solid anaerobic digestion.

It was found that the total content of metals in the feed for co-digestion process was similar or slightly lower for most metals as compared to sewage sludge. The exception was the chromium. Chromium content in the feed increased along with OFMSW dose, because the concentration of Cr in OFMSW exceeded the value observed in SS fivefold

(Table 2). The high concentration of Cr in OFMSW was probably due to the fact that the leachate (used to pulped of OFMSW) contains a large concentration of Cr derived from the broken candle glass which was colored using substances containing chromium.

Digested medium showed an increased total content of all metals comparing to the feed (Table 6). This observation is consistent with the research by Chipasa (2003) and Dong et al. (2013) regarding sewage sludge. The authors found that heavy metals content in digest exceeded the corresponding values in feedstock by about 50%. In the present study, the differences reached approximately 78-132% during digestion of sewage sludge, a maximum increment was observed regarding Cr.

The similar tendency occurred in co-digestion runs (1.R2 and 2.R2) regarding increased total metal content in digest versus feed. However, the differences were in much higher range of 48-517%. The largest variability appeared just for Ni, since its concentration in the phases 1 and 2 exceeded the corresponding value in the feedstock by 261 and 571%, respectively. This was strictly dependent on the OFMSW dose. Interestingly, the lowest increment was observed for Cr and there was no of relationship to OFMSW share.

The increase of metal contents in digest was not proportionally dependent on their initial concentration in feed. However, in most cases introducing OFMSW as a co-substrate to anaerobic digestion led to much greater increases and the metals were much more concentrated in dry sludge as compared to mono-substrate process. The exception was Cd considering both phases as well as Al, Fe and Mn in the phase 2.

The addition of OFMSW to fermenting SS led to an increase in biogas production. It was shown that the 75:25 SS to OFMSW by volume ratio is optimum, assuring effective co-fermentation and increase in biogas production. In turn, the effects obtained using a higher OFMSW proportion (ca. 30%) are comparable with those obtained during fermentation of SS without addition of OFMSW (Lebiocka and Piotrowicz 2012).

The concentration of metals in digest obtained from sewage sludge anaerobic digestion and its co-digestion with OFMSW was in accordance with the compliance limits for agriculture land application (issued by directive 86/278/EWG). However, since addition of OFMSW increases concentration of metals on the dry weight basis, its land application should carefully be considered.

4. Conclusions

It was found that the total content of metals in the feed for co-digestion process was similar or slightly lower for most metals as compared to sewage sludge. The relative abundance of metals was maintained for all runs and followed the general order: Cd < Mo < Co < Ni < Cr < Pb < Cu < Mn < Zn < Fe <Al. The digest showed an increased total content of all metals compared to feed data. The differences reached from 78-132% for sewage sludge and 48-571% using co-digestion.

The increase of metal contents in the digest was not proportionally dependent on their initial concentration in the feed. Co-digestion made metals more concentrated in dry sludge as compared to mono-substrate process, thus the addition of OFMSW was found to determine the digest quality. However, further studies involving metal speciation would have to be undertaken.

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Współfermentacja osadów ściekowych i organicznej frakcji odpadów komunalnych w zakresie stężeń metali ciężkich

Streszczenie

Przedmiotem badań była analiza wpływu zanieczyszczeń pochodzących z organicznej frakcji odpadów komunalnych dodawanych jako kosubstrat do procesu biometanizacji mieszanych osadów ściekowych na stężenia metali ciężkich w osadzie przefermentowanym. Eksperyment obejmował badania modelowe fermentacji mezofilowej (w temperaturze 35ºC) osadów pochodzących z systemu gospodarki osadowej miejskiej oczyszczalni ścieków w Puławach, mieszanych objętościowo w odpowiednich proporcjach z frakcją organiczną odpadów komunalnych przygotowanych i rozpulpionych w odcieku zgodnie z niemiecką technologią BTA. 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 dwóch etapach, z zastosowaniem dwóch różnych dawek frakcji organicznej (osad:frakcja 75:25 i 70:30 obj.). 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 zawartości przed i po procesie współfermentacji. Otrzymane wyniki wskazują, że zawartość metali w mieszaninie zasilającej reaktor w fazach współfermentacji były na podobnym poziomie lub nieznacznie niższe niż w przypadku fermentacji samych osadów ściekowych. Wzrost zawartości metali ciężkich w przeliczeniu na suchą masę w pofermencie wynikał z mniejszej zawartości materii organicznej w fazach, gdy prowadzono proces współfermentacji. Wzrost zawartości metali w pofermencie nie był proporcjonalny do ich zawartości w mieszaninie zasilającej reaktor. Proces współfermentacji powodował, iż zawartość metali ciężkich w osadzie przefermentowanym była wyższa, oznaczać to może, że dodatek organicznej frakcji odpadów komunalnych może mieć wpływ na jakość pofermentu. Dodatkowo, w przyszłości powinny zostać wykonane badania uwzględniające specjację metali.

Słowa kluczowe:
osad ściekowy, organiczna frakcja odpadów komunalnych, współfermentacja, metale ciężkie

Keywords:
sewage sludge, organic fraction of municipal solid waste, co-digestion, heavy metals