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**ASSESSMENT OF PHYSICAL, CHEMICAL AND ENERGETIC
PROPERTIES OF SLUDGE IN INDUSTRIAL AND MUNICIPAL
SEWAGE TREATMENT PLANT**

Abstract

The work presents physical, chemical and energetic properties of sludge from industrial and municipal sewage treatment plant in West Pomeranian Voivodeship. Among many macronutrients, sludge contains much of the following: nitrogen, phosphorus, calcium and magnesium, but little potassium. Total content of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Hg, Zn) was lower than norms admitting sludge for natural, including agricultural use, presented in the Order of Ministry of the Environment¹⁴. Much content differentiation of particular sludge components indicates on the necessity to analyze each portion before its use. The kind of sludge (municipal, industrial) and the way of processing (thickening, drainage, drying) is embodied in differentiation in the content of organic dry matter and total organic carbon. Heat of combustion and calorific value of analyzed sludge oscillates in a very wide scope and the lowest value of indexes were achieved for dried municipal and industrial sludge, whilst higher for thickened municipal sludge and drained one. Sludge, the one after initial thermal processing (i.e. drying) can be used as renewable source of energy. Pearson's linear correlation analysis of sludge has show significant positive linear dependence between calorific value and organic dry matter content as well as total content of carbon and nitrogen for all analyzed kinds of sludge.

Key words: sewage sludge, properties of sludge, chemical composition of sludges, heat of combustion and calorific value of sludge

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INTRODUCTION

Municipal sludge is waste, that develops during daily life processes, work and recreation of country's inhabitants – who are its direct producers, furthermore, it is also a derivative of some industrial processes. Physical and chemical composition of sludge, and especially the content of heavy metals, should be particularly monitored and limited.

Sludge management is subject not only to waste management act, but also to other acts and regulations, that are specific in the way of sludge development, treatment and the scale of environment threat.

National Waste Management Strategy [Journal of Law, 2010, no101 item 1193]. Presupposes that in 2022 in Poland there will be developed ca. 746,00 thousand of Mg d.m. of sludge, i.e. 3 730, 00 thousand of Mg with water content of 80%. Increasing amount of sludge forces designers to search for alternative methods of sludge processing. Therefore, for most of the large agglomeration designs, drying and thermal recycling of sludge is suggested.

Sludge contains organic substance in over 50 percent [Cornel et. al 2011, Czekala 1999, Ndaji et. al 1999, Roca-Perez et al 2009, Shen and Zhang 2003, Stelmach and Wasielewski 2008], so it can be used as renewable source of energy (RSE). For Poland, as a member state of European Union, sludge becomes a very valuable RSE, due to the ecological policy that is imposed according to EU Directive 2001/77/WE as of 27 September 2001.

The goal of this work is to assess physical, chemical and energetic properties of sludge coming from industrial and municipal sewage treatment plant in West Pomeranian Voivodeship.

Material and methods

Analyzed sludge comes from sewage treatment plant localized in West Pomeranian Voivodeship:

- sludge 1 – from a food industry treatment plant (brewery), where dewatering process takes place on a belt press;
- sludge 2 – from a mechanical-biological treatment plant (village), where dewatering process takes place in a sludge bagging machine. In such a sewage treatment plant water plants partially participate in the process of biological sludge treatment;
- sludge 3 – from a municipal mechanical-biological sewage treatment plant (city of 200 000 PE), where dewatering process takes place on a belt press;
- sludge 4a – from a municipal mechanical-biological sewage treatment plant (city of 419000 PE), where sludge undergoes thickening process only;
- sludge 4b – as above, where sludge undergoes dewatering on a belt press;

- sludge 4c – as above, where sludge undergoes dewatering on a belt press, and then is dried in a contact dryer.

Sludge 4a, 4b and 4c come from the same sewage treatment plant, but the samples were taken from different stages of technological processing.

In sludge samples the following parameters were made:

- pH as of PN-91C-04540/05/01,
- dry matter, organic dry matter, dry mineral substance as of PN-EN-02/12879,
- total content of nitrogen, carbon and sulphur with the use of CNS elemental analyzer by Coestech,
- total content of phosphorus as of PN-98C-04537-14,
- total content of potassium and calcium as of PN-ISO 9964/1 and 2,
- total content of heavy metals (Cd, Cu, Cr, Mn, Ni, Pb, Zn) as of PN-ISO 02/8288,
- total content of mercury with the hydride generation method,
- heat of combustion and calorific value as of PN-EN-ISO 9931:2005.

Sludge from the chosen West Pomeranian Voivodeship sewage treatment plants characterize with much differentiation of physical, chemical and technological properties. Physical properties, to which we include: dry matter content, organic dry matter content and mineral matter content, were dependent on the kinds of sludge and the way of its processing.

Mechanical process of sludge, on a belt press, ought to ensure sludge acquisition of dry matter content over 20%. In this study, sludge 1 and 3 met the requirements and contained 21.3 and 22.1 % d.m. respectively, however, sludge 4b failed to reach the limit of over 20% d.m. and contained 17.4% d.m. (Table 1). The lowest content of dry matter (4.43%) had sludge 4a (municipal after thickening), and the highest (95.4%) sludge 4c (municipal after drying).

Organic dry matter content in analyzed sludge ranged from 29.2 to 67.6%. The least of organic substance contained sludge coming from food industry, and the most from agglomeration with 200 000 PE (sludge 3). It has been observed that together with sludge processing, lowering of organic substance content and total carbon took place. Sludge that underwent thickening process only contained 57.2% d.m.o., and after drying process in a contact dryer the content of dry organic substance reduced to 41.0%. Similar relationship appeared for total carbon.

Among chemical properties which determine fertilizer value and usefulness of sludge for soil fertilization and plants manuring, also reaction, content of macronutrients and heavy metals should be included, many of which are essentials micronutrients.

Tab. 1. Physical, chemical and energetic properties of industrial and municipal sludges

Tab. 1. Fizyczne, chemiczne i energetyczne właściwości przemysłowych i komunalnych osadów ściekowych

Type of sludge	Dry matter	Dry organic matter	Dry mineral matter	pH H ₂ O	N	C	S	P	K	Ca	Heat of combustion	Calorific value
	%											
Sludge 1	213	29.2	70.8	6.12	2.45	18.7	0.421	0.721	0.238	0.158	13.83	13.05
Sludge 2	10.9	56.5	43.5	6.85	6.02	39.7	0.724	0.983	1.486	0.998	26.90	26.63
Sludge 3	22.1	67.6	32.4	6.75	7.27	42.3	0.622	1.352	0.434	1.791	31.41	30.63
Sludge _{4a}	4.43	57.2	42.8	6.91	4.82	35.5	0.672	1.294	0.920	0.778	28.10	27.38
Sludge _{4b}	17.4	52.2	47.8	7.07	5.00	32.0	0.934	1.218	0.816	1.602	27.64	26.86
Sludge _{4c}	95.4	41.0	59.0	7.14	3.70	27.9	0.892	1.250	0.552	6.212	21.34	20.21

The lowest pH value marked in water (6.12) had sludge 1, coming from food industry (from brewery) – table 1. Sludge from municipal sewage treatment plants were more alkaline and its pH ranged from 6.85 to 7.14.

The lowest amount of total carbon has been marked in sludge 1 (18.7% d.m.), and over two times more in sludge 2 and 3 (from village sewage treatment plant and from smaller urban agglomeration). Sludge 4 (from large urban agglomeration sewage treatment plant) that underwent thickening and dewatering on belt press, contained similar amount of carbon (35.5 and 32.0% d.m.), and after drying in a dryer the content of this component reduced to 27.9% d.m.

Total content of nitrogen was dependent on kinds of sludge and the way of its processing (Table 1). The poorest amount of nitrogen was in sludge 1 (2.45% d.m.), and the richest was sludge 3 (7.17% d.m.). Sludge 4 coming from different stages of processing in the same sewage treatment plant, similarly to carbon, after thickening (sludge 4a) and dewatering on belt press (sludge 4b) contained almost the same amount of nitrogen (4.82 and 5.00% s.m.), and after drying much less (3.70% d.m.).

Total content of phosphorus, potassium, calcium and sulphur in analyzed sludge ranged in a very wide scope (Table 1). The poorest amount of all mentioned components was in sludge from food industry sewage treatment plant. Total content of phosphorus in sludge 1 was 0.721% d.m., and in other it ranged from 0.983 to 1.352% d.m. sludge from municipal waste usually characterize with a small total content of potassium (ca. 0.50% K d.m.), because this component accumulates in drain water. This study indicates on the fact, that potassium appears in much higher content in sludge, depending on its kind and way of processing. In sludge 1, content of potassium (0.238% d.m.) was lower, and in sludge 3 (0.434% d.m.) it was close to the average of many country studies, and in sludge 2 it was higher (1.486% d.m.) ca. three times. Sludge 4a and 4b had 0,920 and 0, 816% of potassium in dry matter, and 4c almost a half less. Similarly to phosphorus and potassium, the lowest total content of calcium

was found in sludge from brewery (0.158% d.m.), and almost six times higher in sludge 2 (0.998% d.m.). High calcium content also had sludge 3 and 4b (1.791 and 1.602% d.m.), which were sampled for analysis after dewatering on a belt press. Sludge 4a (after thickening) had nearly two times less calcium (0.778% d.m.), and in sludge 4c content of this component increased to 6.212% d.m.

Sludge can be a considerable source of sulphur for plants, which deficiency is noted in soils from over a half of agricultural lands in Poland. Total content of sulphur in sludge from brewery was 0.421% s.m., and in other was higher and ranged from 0.622 to 0.934% d.m.

Total content of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn) in sludge is a very important element of sludge chemical composition. Norms that allow sludge for natural use were determined in Environment Minister's Order [Journal of Law, 2010, no 137 item 924].

Content of cadmium ranged from 0.83 to 1.63 mg·kg⁻¹d.m. (norm 20 mg·kg⁻¹d.m.), which means that it was even 12 to 24 times lower than the norm.

Chrome ranged from 8.42 to 13.4 mg·kg⁻¹d.m., which indicates on its wide variety in flowing sludge. The difference between the lowest content of copper in sludge (229 mg·kg⁻¹d.m.) and the highest (341 mg·kg⁻¹d.m.) was 48.9%. Manganese, that was not included in the norm, ranged from 51,2 to 243,0 mg·kg⁻¹s.m. Sludge dehydration process had influence on the content of this micronutrient. Having analyzed sludge 4a, 4b and 4c it was established that together with the loss of water, content of manganese in sludge was increasing from 66.75 mg·kg⁻¹d.m. (thickened) to 157.0 mg·kg⁻¹d.m. (dried). Content of nickel in sludge also ranged in wide boundaries (from 23.19 to 56.20 mg·kg⁻¹d.m.), but according to the norm, it was over 5 to ca. 13 times lower. Concentration of lead ranged from 25.8 to 39.7 mg·kg⁻¹d.m. and it was much lower than the norm (750 mg·kg⁻¹d.m.), with the use of sludge in agriculture and for ground reclamation for farming purposes (Table 2).

Among analyzed heavy metals, content of mercury in sludge deviated from the norm in the lowest range (16 mg·kg⁻¹d.m. with the use for agriculture and ground reclamation for farming purposes). As for its highest content – 0.901 mg·kg⁻¹d.m. there was 16.6 times less (agriculture use), and with the lowest content – 0,380 mg·kg⁻¹d.m. – 39.5 times. Content of zinc in examined sludge was lower several times from the acknowledged norm. Sludge that come from village agglomeration and smaller urban one (sludge 2 and 3) included less amount of this element (498 and 462 mg·kg⁻¹d.m.), and in other sludge its content ranged from 512 to 536 mg·kg⁻¹d.m.

Tab. 2. Content of heavy metals in industrial and municipal sewage sludge
 Tab. 2. Zawartość metali ciężkich w komunalnych osadach ściekowych

Type of sludge	Cd	Cr	Cu	Mn	Ni	Pb	Hg	Zn
	<i>mg·kg⁻¹d.m.</i>							
Sludge 1	0.83	9.47	259	51.25	23.19	25.8	0.454	536
Sludge 2	0.87	8.42	287	115.5	27.55	28.9	0.387	498
Sludge 3	1.63	13.4	229	243.0	24.10	31.8	0.825	462
Sludge 4a	1.47	10.8	312	66.75	49.10	34.8	0.879	512
Sludge 4b	1.44	10.4	319	146.25	55.67	36.8	0.846	514
Sludge 4c	1.42	9.87	341	157.0	56.20	39.7	0.901	528

The results of the study show, that heat of combustion of all analyzed sludge was higher than calorific value by 1.01 to 5.98% (Table 1). It has been stated, that heat of combustion of sludge coming from food industry was lower (13.8 MJ·kg⁻¹d.m.), and the highest for sludge coming from agglomeration of 200 000 PE (sludge 3) – 31.4 MJ·kg⁻¹d.m.

On the basis of these results, Pearson's linear correlation analysis was carried out between calorific value (dependent measure Y) and the content of organic dry matter, dry mineral matter and total content of carbon and nitrogen.

Highly significant positive linear dependencies between calorific value and the content of dry organic matter and total carbon and nitrogen content was noted for all examined sludge. Correlation coefficients (r), which show the importance of such dependencies, ranged from 0.9242 (for nitrogen) to 0.9811 (for dry organic matter). Whereas analysis of determination and correlation coefficient carried out for dry mineral mass has shown crucial negative dependencies. Together with the growth of dry mineral mass content, calorific value of sludge was becoming notably lowered, determination coefficient was 96.25% (Table 3).

Discussion

Sludge from chosen sewage treatment plants located in West Pomeranian Voivodeship had the characteristics of much differentiation of physical, chemical and technological properties. Physical properties, to which we include the following: dry matter content, dry organic matter content and mineral matter content, were dependent on kinds of sludge and the way of its processing. In studies by Pascual et al. [1997] the content of organic substance in sludge is 39.35%, in study by Li et al. [2009] and Kitzczak et al. [2012] over 41.0% and by Ndaj et al. [1999] and Roca-Perez et al. [2009] over 60%. Whereas, based on own studies, only in sludge coming from food industry sewage treatment plant

less organic substance was found when compared to properties quoted in literature.

Tab. 3. Linear regression equation and linear correlation coefficient value between organic dry matter content (C_{dmo}), dry mineral matter (C_{dmm}), total carbon content (C_C) and nitrogen (C_N) and calorific value C_v [MJ/kg dm] for sludge

Tab. 3. Równanie regresji liniowej i wartość współczynnika korelacji liniowej pomiędzy zawartością suchej masy organicznej (C_{smo}), suchej masy mineralnej (C_{smm}), całkowitą zawartością węgla (C_c) i azotu (C_n), a wartością opałową C_v [MJ / kg sm] dla osadów

Designation	Unit	Regression equation	The correlation coefficient [r]
Dry organic matter	%	$W_o = 0.4639 \cdot C_{dmo} + 0.6186$	0.9811
Dry mineral matter	%	$W_o = -0.4639 \cdot C_{dmm} + 47.011$	-0.9811
Carbon	%	$W_o = 0.7356 \cdot C_c$	0.9493
Nitrogen	%	$W_o = 3.499 \cdot C_N + 7.0305$	0.9242

Presented analysis of macronutrients content in sludge show that sludge is a significant source of nitrogen, phosphorus, calcium and sulphur for plants, and potassium in lesser amount. A study by Dusza et al [2009] shows that concentrations of of main nutrient compounds in the sludge (N, P K) enables classification of this material as suitable for use in agriculture. Simultaneously, it should be noted, that particular components of sludge are widely different dependent on place it comes from and way of processing.

Results of analyses of sludge coming from West Pomeranian Voivodeship sewage treatment plants presented in this work indicate on the fact that the content of nitrogen, phosphorus and potassium are within the range provided by literature [Gondek 2006, Li et al. 2009, Roca-Perez et al 2009]. Having analyzed total content of sulphur in examined sludge, which ranged from 0.421 to 0.934% it has been stated, that it is lower than provided Shen and Zhang [2003] (1.14%), Stelmach and Wasielewski [2008] (1.34%), as well as Werle and Wilk [2010] (1.00-1.50%). Average total content of calcium in sludge is 1.923% and is lower than data provided by Gondek [2006] and Roca-Perez et al. [2009].

Total content of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn) is a very important element of sludge chemical composition. The norms that allow sludge for natural use were specified in the Order of Ministry of the Environment [2010]. Among analyzed heavy metals, there is no that would exceed the norms presented in the Order of Ministry of the Environment [Journal of Law, 2010, no137 itm 924] regarding use of sludge in agriculture (table 2). Having

analyzed literature [Gondek 2006, Li et al. 2009, Roca-Perez et al. 2009, Torii and Lavado 2009, Wei and Lui 2005] it has been stated, that examined sludge from municipal sewage treatment plants contained lower amounts of heavy metals in most cases.

The content of organic substance in sludge influences heat of combustion and calorific value of sludge. Calorific value determines useful thermal effect of combustion, and heat of combustion is higher than calorific value by condensation heat of total water vapor from fumes, that come from gas humidity and hydrogen combustion [Bień 2007]. Based on own studies, sludge heat of combustion ranged from 13.83 to 31.41 MJ·kg⁻¹·s.m and was dependent on kind of sewage treatment plant and stage of its processing. Whereas, Stelmach and Wasielewski [2008] say that sludge heat of combustion is 11.9 MJ·kg⁻¹·s.m., Werle and Wilk [2010], state that from 7.00 to 15.10 MJ·kg⁻¹·s.m., and Murakami et al. [2009] that from 16 to 21 MJ·kg⁻¹·s.m. This indicates the possibility that municipal waste could be used for energetic purposes – as renewable source of energy.

Conclusion

1. Sludge, depending on the way of its processing and its kind, characterizes with a variable content of organic dry matter and total carbon.
2. Sludge is a rich source of macronutrients such as: nitrogen, phosphorus, calcium and magnesium, except for potassium. A wide variety of content of particular sludge components indicate on the necessity to carry out analysis on each sludge sample.
3. Analyzed sludge did not contain excessive amounts of heavy metals.
4. Calorific value of examined municipal waste ranged from 21.34 to 31.41 MJ/kg d.m. This sludge, after initial thermal processing (eg. drying), can be used as renewable source of energy.
5. Linear correlation analysis of sludge has shown a very significant positive linear dependencies between calorific value and the content of organic dry matter with total content of carbon and nitrogen in all examined sludge.

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OCENA WŁAŚCIWOŚCI FIZYCZNYCH, CHEMICZNYCH I ENERGETYCZNYCH OSADÓW POCHODZĄCYCH Z OCZYSZCZALNI ŚCIEKÓW PRZEMYSŁOWYCH I KOMUNALNYCH

S u m m a r y

W pracy przedstawiono właściwości fizyczne, chemiczne i energetyczne osadów pochodzących z oczyszczalni ścieków przemysłu spożywczego i komunalnych województwa zachodniopomorskiego. Spośród makroskładników osady ściekowe zawierały dużo: azotu, fosforu, wapnia i magnezu, a mało potasu. Całkowita zawartość metali ciężkich (Cd, Cr, Cu, Mn, Ni, Pb, Hg, Zn) była mniejsza od norm dopuszczających osady do przyrodniczego, w tym rolniczego wykorzystania, przedstawionych w Rozporządzeniu MŚ. Znaczne zróżnicowanie zawartości poszczególnych składników w osadach wskazuje na konieczność analizowania każdej partii przed ich wykorzystaniem. Rodzaj osadów (z przemysłu spożywczego, komunalne) i sposób ich przerobu (zagęszczanie, odwadnianie, suszenie) znajdowało odzwierciedlenie w zróżnicowaniu zawartości suchej masy organicznej i węgla całkowitego. Ciepło spalania i wartość opałowa analizowanych osadów ściekowych wahała się w bardzo szerokim zakresie i najniższe wartości tych wskaźników uzyskano w przypadku osadu przemysłowego i komunalnego po suszeniu, a wyższe dla osadu komunal-

nego zagęszczonego oraz odwodnionych. Osady, te po wstępnej termicznej przeróbce (np. suszeniu) mogą być wykorzystywane jako odnawialne źródło energii. Analiza korelacji prostoliniowej Pearsona osadów ściekowych wykazała istotne dodatnie prostoliniowe zależności między wartością opałową a zawartością suchej masy organicznej oraz całkowitą zawartością węgla i azotu dla wszystkich badanych rodzajów osadów ściekowych.

Słowa kluczowe: osady ściekowe, właściwości osadów, skład chemiczny osadów, ciepło spalania i wartość opałowa osadów