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Influence of Mesophilic Digestion of Dairy Sewage Sludge on Content of Chosen Heavy Metals and their Fractions

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1. Introduction

The problem of sewage sludge management, which is the inseparable product of sewage treatment, concerns almost each municipal or industrial wastewater treatment plant (WWTP) (Kogut 2014). The requirements, which have to be fulfilled with the use of sludge in agriculture, are mentioned in regulation concerning municipal sewage sludge. The basic criteria is the content of chosen heavy metals both in sludge and in soil, on which sewage sludge can be used. The largest dairy processing plants are located in podlaskie voivodeship. Some of them have WWTPs. That is why the sludge, which is produced during the treatment process, is used in 100% to fertilize soil (Dąbrowski 2010). Except of high content of such elements like nitrogen or phosphorus, sludge includes also a lot of alkaline elements for example sodium, potassium, calcium and manganese, which is very essential in case of the dominance of light and acid soils in podlaskie voivodeship (Dąbrowski 2009). On account of the production specification in dairy industry, the sewage and sludge are deprived of sanitary contamination. That is why, the basic criteria conditioning safe use of sludge from dairy WWTPs, is the total content of heavy metals. It is also important in which fraction metals will be introduced to the environment and to what expend they will be available for the plants. The most mobile are metals occurring in ion-exchange carbon fractions.

To the end of 2012, podlaskie dairy WWTPs used only aerobic digestion of excessive sludge with the use of separate chambers or simultaneously with the process of sewage treatment. On account of the lack of experience connected with co-digestion of excessive and floatation sludge from pretreatment of dairy sewage, the researches of digestion process in laboratory scale were conducted. There were determined many parameters among others reject water and sludge composition. In the paper, there are shown the researches of labile and stable combination of chosen metals in sludge before and after digestion process.

2. Materials and methods

Sewage sludge, which was exposed to anaerobic digestion process in a laboratory installation, came from the sewage treatment plant of Mlekovita dairy cooperative. The average sewage effluent flow was approximately 5893 m^3 per day, while the amount of sludge produced per year reached about 2500 Mg of dry matter. According to the modernization project, the throughput of wastewater treatment plant will increase up to 7500 m^3 per day, while the amount of sludge – up to 3500 Mg of dry matter per year. Sharp rise of sludge amount is the result of high load of BOD_5 in dairy sewage (Dąbrowski 2009). According to the modernization project, the sludge samples were prepared to the research as the mixture of excessive sludge after thickening (70% of input per dry matter) and floatation sludge from pretreatment of dairy sewage (30% of input). The load of chamber for anaerobic digestion assumed to be approximately 0.7 kg d.m./m^3 per day, which is characteristic value for the classical sludge digestion. The research installation in laboratory tests (Fig. 1) was composed of three closed chambers. Each of them with capacity of 10 dm^3 was equipped with stirring and heating system with and control units. The produced biogas was removed by the system of valves. The process was carried out as a *mesophilic* digestion for 20 days. The automatic control system provided to maintain constant temperature of the process and periodic mixing of the chambers contents.

Within the researches connected with the determination of total content and chosen heavy metals fractions, there were conducted five experiment series covering testing of sludge samples during and after digestion process in mesophilic conditions. Stable sludge was dehydrated using a special hydrophobic cloth used in the bag filter press. Metals were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-OES; Varian apparatus VISTA MPX) after sample digestion with concentrated HNO_3. Samples were digested using microwave digestion. The content of Hg was marked with the AMA-254 spectrum analyzer directly through the sample's catalytic incineration in oxygen. In order to check the process of mineralization, the labeling of each sample was confirmed with a certified material for sewage sludge reference BCR-146 R and material for confirming curie and the whole analytical process SPS-SW2. Moreover, blind samples were used to control the limit of quantification. The metals were tested on interference lines: Cd – 214,439 nm, Cr-267,716 nm, Cu- 327,395 nm, Ni-231,604 nm, Pb-220,353 nm, Zn-213,857 nm (PNEN ISO 11885:2009).

Fig. 1. Laboratory scale research installation for anaerobic sewage sludge digestion (source: W. Dąbrowski)

Modified BCR method with a use of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of metals in sludge samples (Tessier 1979, Łukowski 2014, Rao et al. 2008, Shrivastava and Banerjee 2004). Extraction included four stages:

1. Acid soluble and exchangeable fraction (F1) – 1 g of sludge in 100 cm^3 centrifuge tube with 40 cm^3 of 0.11 mol/dm^3 acetic acid was sonicated for 7 min (power – 20 W) at temperature 22 ± 5°C. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. Residue with 20 cm^3 of deionized water was sonicated for 5 min (power – 20 W) and centrifuged for 20 min at 3000×g. Water was discarded.
2. Reducible fraction, bound to Fe/Mn oxides (F2) – to the residue from the first step was added 40 cm^3 of 0.5 mol/dm^3 hydroxylamine hydrochloride fresh solution, pH 1.5, and sonicated for 7 min (power – 20 W) at temperature 22 ± 5°C. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the first step.

3. Oxidizable fraction, bound to organic matter (F3) – to the residue from the second step was added 20 cm^3 of 30% hydrogen peroxide and sonicated for 2 min (power – 20 W) at temperature 22 ± 5°C. Then, the volume of H_2O_2 reduced to approx. 1 cm^3 using water bath. 50 cm^3 of 1 mol/dm^3 ammonium acetate and sonicated for 6 min (power – 20 W) at temperature 22 ± 5°C was added to the moist residue. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the previous steps.
4. Residual fraction (F4) – residual fraction (option) F4 was calculated from the difference between 100% and summarized percentage of other fractions.

Results are represented as arithmetic mean of three replicates. The differences between the obtained values were determined by one-way ANOVA with Tukey's post-hoc test at confidence level $p < 0,05$.

3. Results and discussion

In table 1 there were shown the research results of exploiter of WWTP connected with the content of metals in dairy sludge exposed to aerobic digestion. This way of sewage sludge stabilization will be used to the moment of startup of digestion chambers and the whole modernized installation in order to treat sludge. Sewage sludge produced during the process of dairy sewage treatment is characterized by differentiated content of heavy metals. Its amount is low comparing to the requirements described in regulation concerning municipal sewage sludge and also the characteristic values for municipal WWTP using aerobic and anaerobic sludge digestion. It is proved by the researches of Rosik Dulewska et al. (2005) concerning the composition of sludge from wastewater treatment plant located within the area of Silesia. Admissible values of metals content in sludge, which was used to fertilize soil, were also presented in Table 1.

Table 1. Heavy metals contents [mg/kg d.m.] in aerobically stabilized sludge in Wysokie Mazowieckie

Metal	Pb	Hg	Cu	Cd	Ni	Zn	Cr
Minimum	-	0.06	17.0	-	1.9	99.8	6.6
Maximum	-	0.21	23.3	-	6.01	145.0	18.8
Mean	<12.5	0.17	20.0	<0.375	3.72	119.0	10.04
Maximum for agriculture reuse*	750	16	100	20	300	2500	500

*Regulation Concerning Municipal Sewage Sludge

In Tables 2 and 3 but also on Figures 2 and 3 were shown the authors' research results with the use of laboratory installation (Fig. 1) connecting the process of anaerobic digestion in *mesophilic* conditions as the determination of total forms and metals fractions. Comparing the total content of metals in aerobically digested sludge (Tab. 1) with those aerobically digested (Tab. 2), the similar amount of lead was stated, while in case of the rest of meals, their content was higher after anaerobic digestion. The content of metals in sludge in case of aerobic digestion used in WWTP of Mlekovita was similar to the one after anaerobic digestion conducted in laboratory conditions and it was far lower than the admissible value while the use of sludge as fertilizer. During conducted digestion process, there was observed the decrease of organic matter content from 79,8 to 58% on average. On the basis of the analysis of heavy metals content before and after anaerobic digestion process, there was stated the increase of metals content per dry matter after anaerobic digestion. The following results were reached: substantial increase of total content of copper and nickel, slight rise of zinc, while the content of lead, cadmium, chromium and mercury changed a little (Tab. 3).

Table 2. Total heavy metals contents [mg / kg d.m.] in row dairy sewage sludge and after *mesophilic* digestion.

Parameter	Pb	Hg	Cu	Cd	Ni	Zn	Cr
Before *mesophilic* digestion							
Minimum	1.2	0.005	16.0	1.2	8.0	185.0	4.5
Maximum	5.0	0.12	28.0	1.4	10.4	216.0	5.7
Mean	3.7	0.078	20.0	1.3	10.0	195.0	4.8
After mesophilic digestion							
Minimum	2.1	0.09	70.0	1.4	56.0	238.0	4.4
Maximum	6.2	0.16	89.0	1.7	69.0	268.0	5.2
Mean	4.8	0.14	85.0	1.6	64.0	255.0	4.6
Maximum for agriculture reuse*	750	16	100	20	300	2500	500

*Regulation Concerning Municipal Sewage Sludge 6.02.2015

Table 3. Fractions of heavy metals contents (mean values) [mg /kg d.m.] before and after *mesophilic* digestion

Metal	Fraction	Before digestion	After digestion
Pb	F I	1.6	1.4
	F II	1.5	2.4
	F III	0.6	0.6
	F IV	0.0	0.4
	Total	3.7	4.8
Cu	F I	0.5	0.7
	F II	1.2	1.5
	F III	15.2	44.2
	F IV	3.1	0.2
	Total	20.0	46.6
Cd	F I	0.04	0.07
	F II	0.75	1.24
	F III	0.5	0.26
	F IV	0.01	0.03
	Total	1.3	1.6
Ni	F I	4.4	4.7
	F II	1.6	12.1
	F III	3.4	6.6
	F IV	0.5	0.6
	Total	10.0	24.0
Zn	F I	31.4	20.9
	F II	62.8	86.7
	F III	97.1	144.3
	F IV	3.7	3.1
	Total	195.0	255.0
Cr	F I	1.8	2.6
	F II	1.0	0.6
	F III	1.5	0.9
	F IV	0.5	0.5
	Total	4.8	4.6

F I – Exchangeable, F II – Reducible, F III – Oxidizable, F IV – Residual

The decay of organic matter during the digestion process was the reason of increase of metals content in dry matter of digested sludge. It is proved by the research of municipal sludge digestion conducted by Dąbrowska (2011) and Obarska-Pempkowiak (2003) together with the team researched metals fractions in sludge from wastewater treatment plant of Gdańsk-Wschód, while Chipasa, except of the total content of metals in sludge, also examined their content in sewage on different stage of its treatment. The results of their researches prove the tendency of increase of metals content after anaerobic digestion process (Kangala 2001).

Sewage sludge is valuable organic waste, which should come back into soil, especially to the light and acid soils. However, in case of high doses of sludge used on such types of soils, it is extremely important to determine in them not only total forms of heavy metals but also their fractions. In case of acid soils, the release of metals is faster and they are more available for plants, which is noticed by Wiater and Łukowski (2014). The process of anaerobic digestion caused the limitations of lead, nickel and zinc mobility (Tab. 3, Fig. 2 and 3). In case of these metals, there was observed the decrease of their content in most available fraction F I. Lead, before and after digestion, occurred mainly in F I and F II fraction, but it clearly moved to second fraction combined with oxides and Fe/Mn hydroxides in result of digestion process. Lead content in fraction combined with organic matter decreased. After digestion process, about 9,7% of lead occurred in residual fraction F IV, which is unavailable for plants. The increase of lead in fraction IV is proved by the researches of Dąbrowska and Solis et al., who determined the speciation of metals in sludge from chosen wastewater treatment plant in Spain (Dąbrowska 2011, Solis 2002). Wilk and Gworek (2009) noticed that lead in sludge is more mobile than in soils, which is proved by conducted researches. Lead is the element, which is stored on the surface of fertilized soils, causing the limitations of organic matter decay.

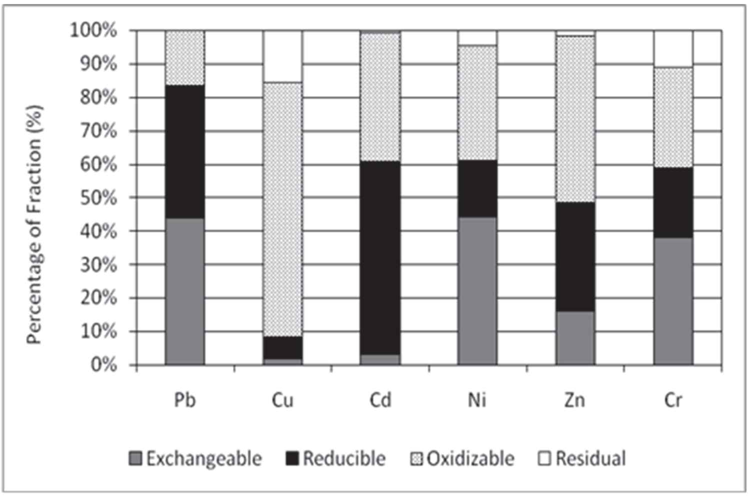

Fig. 2. Fractions of heavy metals in sewage sludge before anaerobic digestion

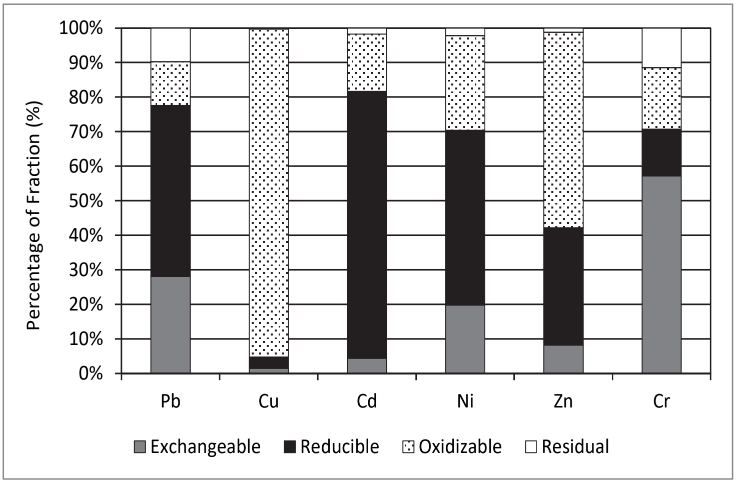

Fig. 3. Fractions of heavy metals in sewage sludge after anaerobic digestion

The process of anaerobic digestion of sludge from dairy WWTP, did not influence copper content in changeable fraction F I, but it decreased its share in fraction F II almost twice from 6,2 to 3,2%. (Fig. 2 and 3). Copper makes stable combination with organic matter, which is proved by the data from References. Ignatowicz (2017) states that copper in municipal sludge occurs mainly in fraction combined with organic matter. Similar conclusions can be found in researches made by Latosińska and Gawdzik (2003), who examined metals fractions in sludge, which was aerobically and anaerobically digested. The digestion process causes sludge thickening and decrease of organic matter, which is proved by copper content in this fraction with the decrease of residual fraction from 15,6% to at least 0,3%. Immobilization of copper is not always favorable, especially when sludge, which is indispensable element for plants, is used to fertilize poor soils.

Cadmium is the most mobile element in soil environment and each external introduction of it can cause the danger of its bioaccumulation. In dairy sludge exposed to digestion, it occurred mainly in reducible fraction F II and fraction with organic matter F III. After digestion process, cadmium was moved from fraction combined with organic matter to residual fraction. In result of anaerobic digestion, the potential mobility of cadmium increased of about 20% (Tab. 3, Fig. 2 and 3). Latosińska and Gawdzik (2003) claim that anaerobically digested sludge includes cadmium mainly in immobile fractions, similarly to the researches of Dąbrowska (2011). In case of nickel, the conducted digestion process decreased its content in the most mobile fraction F I over twice. More nickel was found in reducible fraction F II on charge of changeable fraction F I and fraction combined with organic matter. When the sludge was used on acid soils, less of reducible fraction could move to the changeable one and when soil reaction was higher, this movement was postponed in time. Authors who examined nickel in municipal sludge and composts obtained different results. In analyzed sludge, nickel occurred mainly in fractions combined with organic matter (Ignatowicz 2011, 2017, Wilk 2009).

Digestion process, to the little extent, influenced the zinc content in fraction F II and F III, and it decreased its content in changeable fraction F I almost twice. It proves that zinc mobility is limited by digestion process. Residual fraction F IV slightly decreased from 1,9 to 1,2%.

On the other hand, anaerobic digestion process influenced differently chromium content in particular fractions. This metal mobility increased of about: 20% comparing with the sludge before digestion, 7% – on charge of fraction F II and 13% – comparing with fraction III. Residual fraction did not change. However, different results are given not only by Dąbrowska, who shows the increase of immobile fraction after municipal sludge digestion, but also Gawdzik and Gawdzik (2012) who claim that sludge contains mainly chromium in immobile fraction.

4. Conclusions

1. The total content of heavy metals in dairy sludge both before and after digestion process in *mesophilic* conditions, is low comparing with the requirements of regulation concerning municipal sewage sludge in soil fertilization.
2. In result of aerobic digestion, metals content increased in dry matter, which is mainly caused by the decrease of organic matter content during properly conducted digestion process.
3. The researches of anaerobic digestion of dairy sludge showed slight increase of immobile fraction in case of lead, copper and zinc. The decrease of this fraction was observed in case of cadmium, nickel and the most - chromium.
4. The total content of metals in digested sludge do not show the possibility of their release and availability by plants cultivated on soils fertilized by sludge from dairy comparing wastewater treatment plant. The determination of metals speciation is necessary in case of sludge used to soil fertilization and reclamation. Dairy sewage sludge can be the valuable source of organic matter on light soils occurring in the area of Podlasie region.

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Abstract

In this work, there were shown the research results concerning anaerobic digestion in the *mesophilic* condition. There was done the assessment of content of chosen heavy metals and their fractions in dairy sewage sludge before and after digestion process. The research was conducted with the use of laboratory installation on the base of mixture of excessive and floatation sludge. The process parameters were adopted from the modernization project of dairy sewage treatment plant of Mlekovita cooperative in Wysokie Mazowieckie. The results showed that in case of agricultural use of sludge, the total amount of heavy metals in sludge after anaerobic digestion was sharply lower that the values demanded in regulation concerning municipal sewage sludge. The process of sludge digestion caused the increase of metals content in dry matter of sludge. Metals speciation was determined with the use of scheme in accordance with methodology worked by BRC, which meant indicating four fractions. In case of lead, copper and zinc, the researches of anaerobic digestion process of dairy sludge showed the little increase of immobile fraction. The decrease of metals fraction was observed in case of cadmium, nickel and the clearest – chromium.

Keywords:
heavy metals, fraction, sewage sludge treatment

Wpływ procesu fermentacji mezofilowej na zawartość wybranych metali i ich frakcji w osadzie z oczyszczalni ścieków mleczarskich

Streszczenie

W pracy zaprezentowano wyniki badań dotyczących procesu stabilizacji beztlenowej w warunkach mezofilowych. Dokonano oceny zawartości wybranych metali ciężkich i ich frakcji w osadzie mleczarskim przed i po procesie stabilizacji. Badania prowadzono z zastosowaniem układu laboratoryjnego w oparciu o mieszaninę osadu nadmiernego i flotacyjnego. Parametry procesu zostały adoptowane z projektu modernizacji oczyszczalni ścieków mleczarskich firmy Mlekovita w Wysokiem Mazowieckiem. Stwierdzono, iż ogólna ilość metali ciężkich w osadzie po procesie stabilizacji beztlenowej jest znacznie niższa niż wartości wymagane w rozporządzeniu w sprawie komunalnych osadów ściekowych w przypadku rolniczego wykorzystania osadu. Proces stabilizacji osadu spowodował wzrost zawartości metali w suchej masie osadu. Specjację metali określono za pomocą schematu zaproponowanego przez zgodnie z metodyką opracowaną przez BCR wyodrębniając cztery frakcje. Przeprowadzone badania procesu stabilizacji beztlenowej osadów mleczarskich wykazały niewielki wzrost frakcji niemobilnej w przypadku ołowiu, miedzi i cynku. Zmniejszenie tej frakcji metali zaobserwowano w przypadku kadmu i niklu, i najwyraźniej w przypadku chromu.

Słowa kluczowe:
metale ciężkie, frakcje metali, przeróbka osadów