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Summary of doctoral thesis

INVESTIGATION OF THE EFFECT OF MUNICIPAL SEWAGE SLUDGE STABILIZATION IN VARIOUS WAYS TO THE DEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS PAHS

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Introduction

The formation of a huge number of municipal and industrial wastewater treatment plants, is causing the formation of increasing amounts of waste like sludge. In the mid-90s in the EU a strategy for dealing with sludge, containing organic matter, has been established, which assumed that since 2005, it cannot be deposited in landfills. In the context of the new 2005 EU legislation and the worlds trends, the most popular method of management through storage will have to be discontinued. In the European Union there is a Directive of the European Parliament and Council Directive 2008/98 / EC of 19 November 2008 on waste and repealing certain Directives, according to which all EU member states have to adapt their internal legislation to EU requirements. The ways of using municipal sewage sludge in Poland, as well as legal and administrative basis, are regulated from 8 January 2013 by the Act of 14 December 2012 on waste (Dz. U. 2013 pos. 21, Art. 96 of the Act).

The preferred way for sewage sludge management in the European Union is their thermal utilization, which involves huge financial outlay and is mainly used for large urban sewage treatment plants. Until 2018 the use of thermal methods of sewage sludge disposal is expected to be increased up to 60%. However, there still remain 40% of these deposits, mainly from small urban centers and rural areas, for which the thermal utilization will not be used due to the high costs. In many European Union countries as well as the rest of the World, the sludge, after proper treatment or stabilization, is used for environmental purposes, after considering all the constraints associated with the permissible contents of heavy metals and parasites eggs (WRC of 13 July 2010 on municipal sewage sludge, Dz. U. 2010 No. 137, item. 924)

In 2000, the European Commission has proposed amendments to the Council Directive of 12 June 1986., on the environment protection, in particular the soil, when sewage sludge is used in agriculture, in terms of the organic compounds concentration limits such as PAHs in municipal sewage sludge used nature. Polycyclic aromatic hydrocarbons PAHs are persistent organic pollutants (POPs - Persistent Organic Pollutants), which limits are described in many documents that regulate the emission of pollutants into the soil, water and atmosphere environment. US Environmental Protection Agency (US EPA) placed 16 of these compounds on the list of priority environmental pollutants. These change proposals have not been formally regulated by the European Commission as an appropriate legal instrument for the reduction of PAH content of sewage sludge. The problem of PAHs limits

in Polish sewage sludge still remains unresolved, however, the European trends require that in the near future, this situation will have to be changed due to the harmful nature of these compounds.

The research carried out in the framework of the present dissertation aimed to explain the changes in the content of polycyclic aromatic hydrocarbons (PAHs) in municipal sewage sludge after their chemical, thermal or biological stabilization.

The scope of research:

1. Development of methods for the isolation and determination of polycyclic aromatic hydrocarbons PAHs in sewage sludge samples using gas chromatography with FID detector.

2. Analysis of polycyclic aromatic hydrocarbons PAHs content in raw sewage sludge samples coming from the four selected municipal wastewater treatment plants, using different methods of stabilization: liming, composting sawdust and wood chips, vermicomposting and solar drying.

3. Analysis of polycyclic aromatic hydrocarbons PAHs content in processed, by different methods, sewage sludge samples: liming, composting sawdust and wood chips, vermicomposting and solar drying.

4. Evaluation of the quality and quantity of PAHs detected in raw and processed municipal sewage sludge samples.

5. Evaluation of heavy metal content in the tested samples of raw and processed municipal sewage sludge samples.

6. Evaluation of the impact of the methods of municipal sewage sludge stabilization for PAH content.

7. Evaluation of the phytotoxicity of processed municipal sewage sludge.

The essential aim of this study was to compare four different methods of treatment / stabilization of sewage sludge and to investigate the effect of these processes on the content of selected organic compounds such as PAHs.

Within the framework of doctoral dissertation the thesis have been presented as below:

1. The contents of polycyclic aromatic hydrocarbons PAHs in raw municipal sewage sludge exceed the limit values contained in the European Union legislation for sediments that can be used in agriculture.

2. The processes of composting, vermicomposting, solar drying and stabilization of quicklime cause a reduction of PAH in the treated municipal sewage sludge to the values that meet the conditions of EU legislation. The highest degree of reduction of PAHs were obtained in the method of vermicomposting and solar drying.

3. Processed sewage sludge can be used in agriculture after proper treatment, as an alternative method to thermal sludge disposal, which cannot be cured with thermal process.

According to the European Commission in 2009 for the years 2003-2006 the 37% of the dry weight of the sludge was used in agriculture (in soil). Such use of sewage sludge is very diverse in the Member States and regions. In Wallonia (Belgium), Denmark, Spain, France, Ireland and the UK, more than 50% of sewage sludge is used in agriculture, while in the Member States, such as Finland, Belgium Flemish Region this amount was <5%. In Poland, according to the Central Statistical Office (2014), in 2013 the sewage sludge were used in agriculture - about 14%. The European Commission report estimates show that the projected use of municipal sewage sludge for agricultural purposes can reach 50% for European agglomerations. The use of sewage sludge in agriculture is regulated by EEC Council Directive of 12 June 1986 on the protection of the environment, in particular the soil, when sewage sludge is used in agriculture. This directive defines only the permissible content of heavy metals such as cadmium, copper, nickel, lead, zinc, mercury and chromium in sludge used in soil. In addition, it tells what parameters should the analysis of sludge and soil include, on which sludge is to be used or is used. These are: dry matter, organic matter as TOC, pH, nitrogen, phosphorus, and the above-mentioned metals. In Poland, the issues of agricultural use of sewage sludge is regulated by the Ordinance of the Minister of the Environment of 13 July 2010 on municipal sewage sludge (Dz. U. 2010, No. 137, item. 924). This Regulation specifies the conditions which have to be fulfilled for the agricultural use or other natural eg. in land recultivation. In accordance to this regulation, guidelines deal with the analysis of heavy metals such as Cd, Cu, Ni, Pb, Zn, Hg and Cr, and pathogenic bacteria of the genus Salmonella, and live eggs of intestinal parasites of the genus Ascaris sp., Trichuris sp., Toxocara sp.

Although the Polish legislation have not regulated the issue of PAH in sewage sludge yet, it content should be monitored, due to the mutagenic and carcinogenic properties of PAHs, especially benzo (a) pyrene, one of the strongest known carcinogens. Composting

method increases the PAHs degradation, which is confirmed by the work of other authors. In the study the impact of using different methods of processing sludge used in Poland to the degree of PAHs degradation was also examined.

Materials

Samples for testing of sewage sludge from municipal wastewater treatment plants were collected from the province of Opole. Two of the selected municipal wastewater treatment plants applied liming method quicklime for the stabilization of sewage sludge, next one composted sewage sludge containing sawdust, another municipal treatment plant applied the vermicomposting method using the Vermicultures californian earthworm Eisenia fetida and the last one applied the solar drying of sewage sludge method.

Methods

For the tests of the PAH content in sewage sludge, an own branch of IPMB ICIMB procedure has been used containing chromatographic analysis (gas chromatography with FID detection and MS). The qualitative and quantitative tests of PAHs content in sewage sludge samples have been done. In the samples of processed sewage sludge and soil there have also been tested the physicochemical parameters, according to the WRC of 13 July 2010 (Dz. U. No. 137, item 2010. 924), with the methodology given in Table 1.

Table **1** The physicochemical parameters of the tested soil samples and processed sewage sludge and the methods to determine

Parameters	Test method
pH	Potentiometric method, pH-metry
Dry mass	Weight method PN-EN 15934:2013-02
Organic substance	Weight method PN-EN 15169:2011+Ap1:2012
Total organic carbon TOC	Elementary analysis of TOC by Elementar PN-EN 13137:2004
Nitrogen (N)	Elementary analysis, Analyzer of CHNS by Elementar, PN-EN 15104:2011
TOC/N	Calculation method
Calcium (Ca)	Digestion of the samples in a mixture of acids of HCl:HNO_3 in a volume ratio of 3: 1 (about 200 mg sample dried to constant weight at temperature. 105^{o}C crushed and sifted in a sieve 0.7 mm was subjected to digestion in 12 ml of HCl:HNO_3 (3: 1) on Microwave Pro by Anton Paar. Digested samples have been
Magnesium (Mg)	
Phosphorus (P)	
Potassium (K)	
Cadmium (Cd)	
Copper (Cu)	
Nickel (Ni)	

Lead (Pb)	transferred to a flask vol. 50 ml of deionized water and supplemented to 50 ml, to analyze the solutions diluted 10-fold Analysis ICP-MS Agilent PN-EN ISO 17294-2:2006
Zinc (Zn)	
Chromium (Cr)	
Mercury (Hg)	About 100 mg of solid sample have been analyzed directly on mercury analyzer, Atomic Cold Vapor Absorption Spectrometric method (CVAAS), Analyzer AMA

In order to investigate the effect of the processed sewage sludge on plant growth the phytotoxicity tests have been done. The humus garden soil as an indicator have been used, to which 4 types of processed sludge, in proportions determined in accordance to the RMS for a dose of sewage sludge used in agriculture and land recultivation for agricultural purposes, (Dz.U. 2010 nr 137 poz. 924) have been added. Experiments were carried out for three species: Oats (Avena sativa), White mustard (Sinapis alba) and Garden cuckooflower (Lepidium sativum) for the five types of surfaces: the control soil, soil with composted sewage sludge with sawdust, soil with CaO-stabilized sludge , vermicompost soil, soil with sewage sludge dried by solar energy.

Test results

During both test series, in 2009 and the second series of tests in 2010, in most of the samples of dehydrated raw municipal sewage sludge the presence of the 16 EPA PAHs have been detected. The most common hydrocarbons of PAHs are: benzo(b)fluoranthene and benzo(k)fluoranthene (present in all analyzed samples) and acenaphthylene, acenaphthene, indeno(1,2,3-cd)pyrene, dibenz(a, h)anthracene, benzo(g, h, i)perylene (present in over 90% of samples). For the most rare of PAHs, in sediment samples tested, we can include benzo(a)pyrene, which due to its carcinogenic impact is considered to be an indicator of PAH prevalence. Benzo(a)pyrene have been found in 14 tested samples, including all raw sludge samples collected before the solar drying process.

The highest concentrations of 16 PAHs in dry mass of sewage sludge samples have been found for samples of raw sludge collected in 2009 in the sewage treatment plant, using composting with the addition of sawdust (rural municipality) - from 19.48 to 516.82 mg/kg dm. In these sediments the presence of phenanthrene in very high concentrations has been revealed, respectively 491.54 mg kg dm in the first sample, and 289.52 mg/kg dm in the second sample. These are, however, two isolated instances with such a high content

of phenanthrene determined. Slightly lower concentrations of 16 PAHs have been found in raw sewage sludge samples from the municipal sewage treatment using the stabilisation with quicklime - from 10.71 to 110.12 mg/kg dm. Then, in order to lower and lower concentrations the sewage sludge from using the method of vermicomposting have been placed - from 10.06 to 25.29 mg/kg dm and sludge from drying by solar energy - from 4.16 to 10.02 mg/kg dm.

In both methods, composting with sawdust and stabilization of CaO, vermicomposting and solar drying have reduced levels of PAH. PAH concentrations in sewage sludge after composting with sawdust are much lower than the concentrations of these compounds in the raw sewage sludge change from 0.04 to 5.04 mg/kg dm. Much lower concentrations have been determined in a sample of sewage sludge compost, taken after 1 year of aging on the compost pile. In this sample the 6 hydrocarbons in concentrations ranging from 0.04 to 0.32 mg/kg dm have been determined. In the sewage sludge stabilizing by quicklime (CaO) all of the sixteen PAHs have been found. The sum of 16 PAHs concentrations are within the range of 1.25 to 74.92 mg/kg dm. In the vermicompost samples concentrations of 16 PAHs ranged from 1.15 to 5.20 mg/kg dm, and in samples dried by solar energy from 0.56 to 2.92 mg kg dm.

Analysed processed sewage sludge are characterized by variable amounts of heavy metals, which limits are contained in Regulation (Dz. U. No. 137, item 2010. 924). The highest concentrations of heavy metals, such as copper, nickel, lead, zinc and chromium are reported in sewage sludge dried by solar energy. Their concentration (mg/kg dm) was as follows: copper - 155, nickel - 30.3, lead - 20.6, zinc - 738 and chrome - 42.2, however, does not exceed the limit values according to the RMS. The highest concentrations (mg/kg dm) of cadmium - 1.66, mercury - 5.50 and also lead - 20.7 have been found in the sewage sludge after composting with sawdust addition, and they also did not exceed the limit values according to the RMS on July 13, 2010. The highest calcium content - 22.9 g/kg dm, as expected, in the sewage sludge stabilized CaO have been found, and the lowest - 12.0 g/kg dm in vermicompost. The high calcium content - 20.9 g/kg dm was also recorded in the sewage sludge dried by solar energy. Magnesium in the highest concentration - 7.59 g/kg dm in the sediment dried by solar energy have been determined. The lowest magnesium concentration have been found in the vermicompost sample - 2.79 g/kg dm. The test samples of processed municipal sewage sludge contain the suitable amounts of nitrogen, phosphorus

and organic carbon.

Based on phytotoxicity tests, the following indicators: percentage inhibition of seed germination IG, the percentage inhibition of root growth and the rate of germination IR have been defined. For two representatives of the family of dicotyledonous plants, White mustard and Garden Cuckooflower, there was no negative effect of the addition of four processed sewage sludge to the soil. For the Oats, negative effects of soil containing three types of processed sludge: CaO-stabilized sludge and vermicompost (GI = 88%) and sludge composted with sawdust (GI = 80%) have been found. For the sample dryed by solar energy the GI index was equal to 107%.

Discussion

The obtained results allow to assess the impact of using different methods of stabilization or processing of sewage sludge to changes and concentrations of polycyclic aromatic hydrocarbons PAHs. In addition, it has been determined the extent to which municipal sewage sludge contaminated with compounds of PAHs and which of the proposed methods of sludge processing seems to be the most effective in their reduction. Elementary analysis executed in addition to the content of dry matter, organic matter, TOC, the contents of nitrogen, phosphorus, calcium, magnesium, and metals (cadmium, copper, nickel, lead, zinc, mercury, chromium), allowed to evaluate the applicability of the processed sewage sludge for fertilizer. Furthermore, phytotoxicity tests made it possible to assess what is the impact of the use of sewage sludge on their diverse processing plant growth.

In most of the samples of raw municipal sewage sludge the quantities of identified polycyclic aromatic hydrocarbons PAHs exceeded the acceptable limit of 6 m/kg dm deposit for the sum of 11 PAHs, according to WD 2000. Raw sewage sludge cannot be directly applied to the soil because of the risk of contamination by pathogens and pathogenic microorganisms. In sludge samples from four different municipal sewage treatment plants tested in this work, PAH significantly differ from each other, which confirms that the composition mainly depends on the waste-water delivered to the treatment plant. Significant differences exist between the concentrations of PAHs in sewage sludge coming from rural areas, and samples from small towns to large urban agglomerations.

A significant decrease in the studied PAHs in sediment samples processed four test methods have been observed. For all 16 PAHs the average percent reduction was calculated, in order of highest to vermicomposting sewage sludge - 87.7%, for the solar drying method -

84.3%, for the method of composting sawdust - 80.1%, and the lowest for the method hygenisation quicklime - 78.6%. The study shows, that due to the content of benzo (a) pyrene in stabilized sewage sludge, they do not constitute a major threat to the soil environment.

Results of physicochemical tests of processed sewage sludge that have been carried out, show that regulations governing the permitted content of metals in sewage sludge used for environmental purposes have been fulfilled (Dz.U. 2010 nr 137 poz. 924). The study clearly allow us to conclude that the treated municipal sewage sludge also meet the condotions of organic fertilizers in solid form according to Dz.U. 2008 nr 119 poz. 765.

Conclusion

1. Raw sewage sludges contain large amounts of polycyclic aromatic hydrocarbons, including benzo (a) pyrene, and the quantity and quality depends on the composition of the wastewater treatment plant discharges. PAHs qualitative composition is different for rural wastewater treatment, municipal sewage treatment plant and a large city. This largest treatment plant are often discharged with waste water from industrial areas.

2. After stabilization of sewage sludge in each of the 4 tested methods of degradation of PAHs was found, which can be ranked as follows:

vermicomposting - 87.7%,> Solar drying - 84.3%> Composting with sawdust - 80.1%> hygienisation quicklime - 78.6%.

3. Concentrations of PAHs in the processed sludge which were determined, in most cases meet the criteria proposed in the document WD 2000, which allows 6 mg / kg dry mass for the sum of 11 PAHs in sewage sludge used for agricultural purposes, the concentration

4. Concentrations of PAHs in processed sewage sludge samples by four different methods do not meet the proposals of the European Commission from 2010 (WD 2010) of limits for the sum of concentrations PAHs in the amount of 0.4-0.8 mg / kg dry mass, which confirms the results of research of processed sewage sludge in other European countries, as well as all over the world

5. Due to the carcinogenic and mutagenic properties of benzo (a) pyrene, it should be required to monitor concentrations of PAHs in sewage sludge used for agricultural purposes.

6. Processed sewage sludges meet the conditions of the Regulation of the Minister of the Environment of July 13, 2010, Annex 1 (Dz.U. 2010 nr 137 poz. 924), on the permissible

content of heavy metals in municipal sewage sludge, the requirements for organic fertilizers in solid line of Dz. U. 2008 nr 119 poz. 765 and the guidelines of the Council Directive 86/278 / EEC of 12 June 1986., on the protection of the environment, in particular of the soil,in the case of the use of sewage sludge in agriculture, allowing you to treat it as a full-fledged product with nourishing soil.

7. Processed municipal sewage sludge have no toxic impact for Dicotyledonous plants of the genus mustard and cuckooflower, while causing (except for the dried precipitate by solar energy) limited growth retarding action of monocotyledonous plants of the genus oats.

8. Because of the potential risk for human life and health it should be pursued the use of processed sewage sludge mainly for land recultivation, landscaping and fertilizing eg. energy crops.