

Possibility of Producing Granulated Organic-Mineral Fertilizers from Some Municipal and Industrial Wastes

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Introduction

One of the main factors determining soil fertility and fecundity is organic and mineral fertilization. Nowadays, however, many unfavourable occurrences in the Polish fertilizers management can be observed, including:

- decrease in livestock, thus, in production and usage of natural fertilizers (manure, liquid manure),
- low usage of NPK fertilizers (132.9 kg·ha⁻¹ in the crop year of 2013/14) resulting from increasing prices of raw materials and mineral fertilizers,
- reduction or cessation of soil liming (consumption of CaO was 48.0 kg·ha⁻¹ in the crop year of 2013/14) causing their significant acidification (over a half of the area of arable soils is highly acidic and acidic); assimilability of some plant nutrients decreases in acidic soils (e.g., phosphorus, boron, molybdenum), and some of them transform into highly active forms (e.g., cadmium, manganese, zinc) that, in excess, are detrimental for plants, additionally, soil's acidity inhibits the development of microorganisms taking part in transformation of organic matter as well as in transformation of plant nutrients,
- favourable pro-ecological changes that resulted in lowering the sulphur emission to the environment; although, this also led to shortages of this macronutrient in soils and to the need of sulphur supplementation through fertilization,
- introduction of perennial plants to cultivation intended for production of energy that can lead to soil degradation,
- changes in the structure of crops and too frequent cultivation of the same plant species on a certain field (e.g., corn cultivation for a biogas plant).

The above-mentioned circumstances of the fertilizers management and broadly defined agricultural engineering inspire searching for new sources of materials and substances – both enriching the soil in the organic matter and plant nutrients, and deacidifying soils – that would be cheap, safe for the environment, and giving positive economic outcome.

Attention have been brought to the possibility of using some municipal and industrial wastes for fertilization and recultivation of soils after processing them into organic, organic-mineral, and deacidifying fertilizers, and into plant conditioners.

Sewage sludge

Sewage wastes are produced in industrial plants during production processes and in municipal services management. The wastes are discharged to a sewage treatment plant where they are subjected to the waste treatment processes. In effect, treated water is obtained that can be used in production processes or it can be discharged to watercourses and water bodies; additionally, sewage sludge is created. Sewage sludge is characterised by diverse physical and chemical properties and different sanitary-hygienic condition.

Municipal Sewage Sludge

Municipal sewage sludge contains organic matter and plant nutrients what suggests a possibility of using it for fertilization. It can also contain excessive amounts of some heavy metals, organic compounds of the type of polycyclic aromatic hydrocarbons; it can be also contaminated with bacteria of the genus *Salmonella* and living eggs of the alimentary tract parasites (*Ascaris* sp., *Trichuris* sp., *Toxocara* sp.). That is why, before making the decision on using the municipal sewage sludge for fertilization or recultivation, its physical and chemical properties, and contamination with pathogenic microbes need to be analysed, and then, according to the the relevant national legislation – Regulation of the Minister of Environment (Journal of Laws, 10.137.924), it is necessary to subject it to the processes of hygienisation and stabilisation. This aims at receiving municipal sewage sludge with properties that would not cause environmental contamination, while, in contrary, its effects will contribute to improving soil fertility and increasing the plant yield efficiency.

Table 1 shows chemical properties of the municipal sewage sludge from different localities and according to different authors, and the Table 2 shows the heavy metals limits of contents in the sewage sludge to be used in agriculture and to recultivate soils, according to the Regulation of the Minister of Environment (Journal of Laws, 10.137.924).

Analysis of the data (Tab. 1 and 2) allows to conclude that the studied municipal sewage sludge did not contain excessive amounts of heavy metals. Its pH values were around neutral and it contained diverse amounts of organic matter and plant nutrients. The N:P:K ratio of the municipal sewage sludge indicates low content of potassium in comparison to nitrogen and phosphorus. Intending the municipal sewage sludge for plant fertilization requires addition of potassium to the sludge or to the soil in a form of potassium mineral fertilizers (Tab. 1).

Microbiological analysis of the municipal sewage sludge (Tab. 1) showed that it did not contain bacteria of the genus *Salmonella* nor living eggs of the alimentary track parasites.

Considering the data on the chemical composition of the municipal sewage sludge it has to be concluded that each batch of the sludge intended for fertilisation requires chemical analysis and controlling its sanitary-hygienic condition.

The possibility of using the municipal sewage sludge for fertilization and its positive influence on the fertility and fecundity of soils was noticed by Baran (2004) [1], Baran et al. (2008) [2], Drab et al. (2004) [7], Kaczor et al. (2006) [10], Krzywy et al. (2000) [15], Krzywy (2007) [16], Rosik-Dulewska (2008) [27], and Stankowski and Krzywy (2004) [32].

Before introducing to soils or land, the municipal sewage sludge has to undergo stabilisation and hygienisation. The most common method of stabilisation and hygienisation of the municipal sewage sludge is composting. In the opinion of Baran (2004) [1], Czekala (2008) [5], Dach and Zbytek (2005) [6], Karoń and Pietr (2006) [12], Klasa et al. (2006) [13], Krzywy et al. (2011) [17], Krzywy-Gawrońska (2006) [22], Rosik-Dulewska (2008) [27], Sikorski and Matyja (2008) [30], and Wysokiński and Kalembasa (2006 and 2009) [34, 35]

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composting the municipal sewage sludge leads to obtaining nutritious organic fertilizer. Composting should be held with the addition of structure-forming components in order to increase the airiness of the compost mass, receive optimal C:N and C:P ratios, keep moisture on the level of 40–60%, increase the content of organic carbon and plant nutrients, lower the content of heavy metals, and introduce microorganisms decomposing the organic matter.

The following components, meeting the required conditions, can be chosen: straw of cereals, bark, sawdust, wood chips, ashes of brown coal and biomass, selected municipal wastes, peat, and others. Addition of the structure-forming components should comprise 20 to 30% calculated for the dry matter of the mixture intended for composting.

Traditional composting of the municipal sewage sludge takes from 6 to 8 months; while, significantly shorter amount of time – when conducted with industrial methods. For instance, the process of composting in the biostimulator with the DANO method lasts only 36 hours. Next, the compost mass is subjected to ripening in a pile for 6 weeks. Composting the municipal sewage sludge with the GWDA method comprises of three stages. In the first stage of the anaerobic composting, the temperature in the pile rises to about 30–35°C. The composted mixture should be kept in the anaerobic conditions for minimum three weeks. In the second stage of aerobic composting, the composted mixture should be kept in aerobic conditions for minimum 12 days. In the GWDA method of composting, the aerobic process has been modified by the usage of the aerating device comprising of perforated steel pipes, arranged in the piles. After the aeration, lasting for about 2 weeks, the piles are dismantled and the compost is passed to ripening. The ripening process lasts about 4 weeks (Krzywy 2007) [16].

Further analysis showed that using the municipal sewage sludge, fertilizing mixtures can be created, from which, after the process of granulation, granulated organic-mineral fertilisers are obtained (Krzywy et al. 2012) [18].

Industrial Sewage Sludge

The processes of production in the industrial plants create sewage wastes that are then subjected to the waste treatment processes and, in effect, industrial sewage sludge is created. Some can contain plant nutrients. It can be used to improve the indicators of the fertility and fecundity of soils. Chemical composition of the industrial sewage sludge is more stable than the municipal sewage sludge. This is a result of the chemical composition of individual raw materials and technologies used in the production process. Table 3 shows chemical properties of the industrial sewage sludge from the plant producing compound mineral fertilizers, urea and titanium dioxide. The samples were collected after 1, 2, and 6 months since deposition of the industrial sewage sludge on the pile.

Analysing the data contained in the Table 3 allows to conclude that the industrial sewage sludge had alkaline pH and contained nutrients necessary for the growth and development of plants. The alkaline pH of the industrial sewage sludge resulted from adding the lime slurry $[\text{Ca}(\text{OH})_2]$ during the process of waste treatment for stabilisation and neutralisation of its acidic pH. The alkaline pH of the industrial sewage sludge indicates the possibility of using it for deacidification of most soils.

The total content of heavy metals in the industrial sewage sludge was lower than set by the standards for the municipal sewage sludge (Tab. 2). Thus, there is no possibility of contamination of soils and the environment.

Usually, from certain production plant also domestic wastes are discharged to the industrial wastes. Therefore, when intending the industrial sewage sludge for fertilization, they need to be subjected to sanitary-hygienic control as well as determination of bacteria from the genus *Salmonella* and living eggs of the alimentary tract parasites (Krzywy and Moździerz 2013) [20, 21].

Table 1

Chemical characterisation of municipal sewage sludge

Determined parameter	Location of sampling the municipal sewage sludge						
	Ślawno (Frankenstein 2001)	Zgorzelec (Drab and Derengowska 2003)	Łobez (Krzywy et al. 2005)	Stargard Szczeciński (Krzywy et al. 2012)	Stargard Szczeciński (Krzywy et al. 2013)	Ślupsk (Stachyra 2012)	Gryfice (Goch 2011)
pH _{H₂O}	7.0	7.7	7.3	7.5	7.2	8.2	9.40
Dry matter %	17.8	23.8	20.2	22.5	23.2	23.9	22.9
Total content in g·kg ⁻¹ d.m.							
organic C	329	553	397	422	445	not determined	477
Nitrogen	46.7	37.4	37.4	43.0	40.1	43.7	42.5
Phosphorus	18.6	23.8	20.5	21.6	20.5	21.2	14.3
Potassium	5.10	10.5	8.40	5.10	3.50	4.20	3.25
Calcium	16.7	61.0	25.0	24.5	24.5	28.8	14.2
Magnesium	3.00	12.0	2.60	2.90	2.65	3.89	4.80
Sulphur	8.30	not determined	9.20	5.95	6.00	3.28	not determined
N:P:K ratio	1.0:0.39:0.19	1.0:0.64:0.27	1.0:0.55:0.22	1.0:0.50:0.12	1.0:0.51:0.09		
Total content in mg·kg ⁻¹ d.m.							
Cadmium	4.16	6.90	2.78	2.95	3.20	1.32	0.94
Copper	170	210.0	60.0	120.0	115	180.9	110.2
Chromium	not determined	27.0	not determined	56.0	53.0	33.0	7.97
Nickel	33.4	34.0	30.3	24.3	24.4	15.6	10.5
Lead	55.7	130.0	56.4	59.7	58.8	30.4	161.7
Zinc	1460	1525	415	1080	1040	965	1025

Table 2

Limits of contents of heavy metals in the municipal sewage sludge according to the Regulation of the Minister of Environment (Journal of Laws, 10.137.924)

Metals	Limit of content in relation to intended usage, mg·kg ⁻¹ d.m.	
	for agriculture and recultivation of soils for agricultural purposes	for recultivation of areas for purposes other than agricultural
Cadmium	20	25
Copper	1000	1200
Chromium	500	1000
Nickel	300	400
Lead	750	1000
Zinc	2500	3500
Mercury	16	20

Table 3

Chemical composition of the industrial sewage sludge originating from the plant producing compound mineral fertilizers, urea and titanium white (Krzywy and Krzywy-Gawrońska 2012) [17]

Sampling time since deposition on the pile	pH in H ₂ O	dry matter (d.m.) (%)	Total content, g·kg ⁻¹ d.m.							Total content, mg·kg ⁻¹ d.m.				
			N	P	K	Ca	Mg	S	Cd	Cu	Pb	Ni	Zn	
			1 month	8.39	25.3	1.32	6.50	0.92	4.69	1.36	1.87	0.80	22.5	54.5
2 months	8.23	30.6	1.24	6.45	0.90	4.58	1.34	1.82	0.78	22.3	54.0	150	120	
3 months	8.20	31.6	1.15	6.38	0.88	4.60	1.35	1.76	0.70	22.0	50.0	152	118	

Studies of Krzywy *et al.* (2012, 2013) [17÷19] indicate that the industrial sewage sludge originating from the plant producing compound mineral fertilizers, urea and titanium dioxide can be used for production of compost as well as fertilizing mixtures from which granulated organic-mineral fertilizers can be obtained.

Ashes

After combustion of brown coal and plant biomass for the production of power in heat and power plants, ashes remain. Among a number of methods of their utilization or ways of making use of them, attention has been brought to using them for the purposes of fertilization. Ashes in general are characterised by the lack of organic substances, nitrogen, and their chemical composition is very diversified. Some ashes contain very high amounts of calcium and have alkaline pH. Therefore, previous studies concerned mainly the usage of ashes for deacidification of soils. However, due to the dusty consistency of ashes, their direct application to soils presents some difficulties connected to the possibility of dusting neighbouring fields and negative influence on the environment. That is why, studies were undertaken on the possibility of introducing to ashes components containing organic matter and some plant nutrients in order to receive fertilizing mixtures. These mixtures were subjected to the process of granulation. Among many groups of ashes, ashes from brown coal and plant biomass are the most suitable for the purpose of fertilization.

Ashes from Brown Coal

In Poland, 5 centres mining brown coal for the production of power are operating. During combustion of brown coal, technological wastes are created in a form of boiler slag, and bottom and fly ashes. Fly ashes are accounted to the group of noxious wastes, however, they do not cause risk to human nor animals and environment (Berg and Feneborn 2006 [3], Gawlik *et al.* 2007 [9], Stolecki 2005 [33]). Stolecki (2005) [33] thinks that fly ashes have the highest share in the by-products of the brown coal combustion. They comprise about 90% of all the wastes.

It is estimated that in Poland about 6.5 million tonnes of fly ashes from brown coal are created (Kafanek and Szczygielski 2006 [11]).

The ashes from brown coal, basing on their activity and content of the calcium oxide (CaO), are divided into the following groups:

- ashes inactive or of very low activity, when containing less than 3.5% of CaO,
- ashes of low activity, when containing from 3.5% to 7.0% of CaO,
- active ashes, when containing from 7.0% to 10.0% of CaO,
- ashes of very high activity, when containing over 10% of CaO (Bolt and Byczkowski 2002 [4], Skalmowski *et al.* 2006 [31]).

There are also other criteria of dividing the fly ashes from brown coal.

The fly ashes from brown coal have unstable chemical composition that depends, to a large extent, on the place of origin of the brown coal, the method and temperature of combustion (Galos and Uliasz-Bocheńczyk 2005 [8], Pilarski *et al.* 2008 [24]).

Table 4 shows composition of ashes from brown coal from different sources.

Table 4

Content of some macronutrients in the fly ashes from combustion of brown coal originating from different heat and power plants (Ostrowski 2011 [23])

Parameter, %	Ashes origin				
	Bełchatów I	Bełchatów II	Bełchatów III	Pątnów	Turów
SiO ₂	33.5	40.2	45.2	42.5	35.3
Al ₂ O ₃	19.2	24.0	20.8	6.37	21.6
FeO ₃	5.37	5.93	4.58	4.83	5.62
CaO	31.2	22.4	20.1	30.1	20.0
MgO	1.84	1.27	1.50	5.03	1.56
SO ₃	4.33	2.49	2.50	8.24	8.01
K ₂ O	0.11	0.20	0.19	0.45	1.38
Na ₂ O	0.31	0.15	0.23	0.17	1.05
Free lime	2.21	1.86	1.21	7.60	6.20

Data contained in the Table 4 indicate that the fly ashes from different brown coals contain some compounds necessary for the fertilization of soils and plant nutrition. They had high content of CaO and SO₃. These ashes are suitable primarily for deacidification of soils; transformation of some plant nutrients from unassimilable forms into the forms assimilable for plants occurs (e.g., P). Some heavy metals transform from soluble forms into the forms unassimilable for plants (e.g., Cd, Pb, and Mn).

In connection to high deficiency of sulphur in a lot of arable soils, ashes from brown coal can decrease its shortage. Contents of other plant nutrients (MgO, K₂O, and Na₂O) were not very high. These macronutrients should be supplemented with mineral fertilisers.

Studies of Krzywy *et al.* (2012) [18] indicate that the ashes from brown coal originating from the heat and power plant Adamów had alkaline pH (pH in H₂O – 12), contained 98% of dry matter, did not contain organic matter nor nitrogen. The contents of macronutrients (g·kg⁻¹d.m.) were as follows: P – 24.8; K – 5.76; Ca – 225; Mg – 12.0; S – 2.95, and the contents of some heavy metals (mg·kg⁻¹d.m.) were as follows: Cd – 1.95; Cr – 12.5; Cu – 25.6; Ni – 12.0; Pb – 14.2, and Zn – 220. These data are similar to those presented in the Table 4. The heavy metals content in ashes from brown coal does not cause pollution of the environment and can be successfully used to produce fertilizing mixtures and granulated organic-mineral fertilizers.

Ashes from Plant Biomass

Next years, the renewable sources of energy will comprise 20% of the Polish energy production. One of the directions of obtaining the energy from the renewable sources is cultivation of plants intended for the power production, and then subjecting them to the process of combustion. As a result, ashes are created. Currently

different methods of utilisation or making use of the ashes from the combustion of plant biomass are considered. One of the ways is to use them for fertilization.

Plants intended for power production differ regarding their nutritional and fertilization requirements. Their yields and chemical composition are different. Chemical composition of plants intended for power production highly depends on the fertilization system.

Table 5 compares some of the macronutrients in the ashes from the biomass of plants intended for power production and from barley and wheat straw.

Table 5

Contents of some macro- and micronutrients in the ashes from the biomass of plants intended for power production and cereal straw, %

Content, %	Sugar miscanthus	Prairie cordgrass	Virginia mallow	Jerusalem artichoke	Multiflora rose	Barley straw	Wheat straw
	Kowalczyk-Juško (2009) [14]					Piekarczyk et al. (2011, 2013) [26, 25]	
Humidity	7.70	13.5	8.30	9.70	14.6	-	-
Silica SiO ₂	77.9	66.1	3.20	6.80	6.74	-	-
Iron Fe ₂ O ₃	1.33	0.98	0.76	0.51	1.69	0.32	0.45
Aluminium Al ₂ O ₃	2.06	0.85	0.48	0.46	0.81	-	-
Manganese Mn ₃ O ₄	0.09	0.10	0.05	0.05	0.09	0.10	0.06
Titanium TiO ₂	0.06	0.04	0.04	0.02	0.04	-	-
Calcium CaO	8.35	14.3	36.7	18.8	32.0	11.2	9.08
Magnesium MgO	0.82	2.30	5.34	1.06	7.85	0.86	0.88
Sulphur SO ₃	2.21	4.63	2.42	1.85	3.50	-	-
Phosphorus P ₂ O ₅	1.87	2.96	4.85	3.69	16.5	4.74	1.33
Sodium Na ₂ O	0.46	0.88	0.80	0.54	0.82	-	-
Potassium K ₂ O	2.66	4.97	14.3	25.8	13.0	29.8	9.04
Strontium SrO	0.022	0.04	0.10	0.09	0.12	-	-
Chlorides Cl	-	0.25	0.24	4.74	1.00	-	-

The data (Tab. 5) indicate that ashes from the biomass of individual plant species and cereal straw contain macronutrients and some micronutrients necessary for proper growth and development of plants. However, the content of these nutrients in ashes from individual plants and cereal straws is highly variable. The highest content of calcium and magnesium was found in ashes of the Virginia mallow and multiflora rose (35.7 and 32.0% CaO, and 5.34 and 7.85% MgO). In the ashes of other plants, the content of CaO ranged from 8.35 to 18.8%, and MgO from 0.82 to 8.30%. Significantly more phosphorus (P₂O₅) was in the multiflora rose (16.5%) in comparison to ashes from other plants and straws, where its content ranged from 1.87 to 4.85% P₂O₅. The highest content of potassium was found in the spring barley straw (29.8%), less in the Jerusalem artichoke (25.8% K₂O), the Virginia mallow (14.3% K₂O), multiflora rose (13.0% K₂O), wheat straw (9.04%), and significantly lower content was found in the ashes from the prairie cordgrass (4.97%) and sugar miscanthus (2.66%). Content of sulphur in individual energetic plant species ranged from 1.85 to 4.63% SO₃, iron from 0.51 to 1.69% Fe₂O₃, and in the cereal straw from 0.32 to 0.45%, manganese in the energetic plants ranged from 0.05 to 0.10% Mn₃O₄, and in the straw from 0.06 to 0.10%, and titanium in the energetic plants ranged from 0.02 to 0.06% TiO₂.

The content of silica (SiO₂) in the ashes from individual energetic plant species had to be also noticed, its highest content was found in the ashes from sugar miscanthus and prairie cordgrass (77.9 and 66.1% SiO₂).

Also wastes originating from the wood industry are used for energetic purposes. These wastes can be divided into two groups: contaminated and uncontaminated with different kind of chemical compounds during production. Chemical composition of wastes from the wood industry is highly variable. Therefore, in order to determine their suitability for fertilization, each batch of wastes from the wood industry need to undergo chemical analyses.

Methods of Preparing Organic-Mineral Fertilising Mixtures for the Production of Granulated Fertilizers

The conducted chemical characterisation of the analysed wastes indicates that it is possible to use them to produce fertilizing mixtures improving the indicators of the soil fertility and fecundity as well as the quality of yield obtained from plants.

In further studies attempts were made to produce granulated organic-mineral fertilizers from the created fertilizing mixtures. The studies had the following assumptions:

- chemical composition of the organic-mineral mixtures (containing macronutrients and contaminations) should comply with the standards contained in the Regulation of the Minister of Agriculture and Rural Development (Journal of Laws, 08.119.765). This indicator has to be followed when determining the of material composition of the organic-mineral mixtures intended for granulation,
- the N:P:K ratio of the organic-mineral mixtures should be similar to 1.0:0.4:1.0. It is also possible to elaborate the formula of material and chemical composition of the fertilizing mixtures for the production of granulated organic-mineral fertilizers intended for fertilization of specialized plants or recultivation of soils,
- in order to obtain optimal N:P:K ratio of the granulated organic-mineral fertilizers as well as fast and proper influence on the fertility and fecundity of soils, mineral straight fertilizers containing nitrogen, phosphorus and potassium can be added to the fertilizing mixtures produced from wastes. The amount and kind of mineral fertilizers should not exceed 25% of the total amount calculated for dry matter of the fertilizing mixture. The contained macronutrients originating from the mineral fertilizers will enable faster growth and development of plants at the beginning of their vegetation. Moreover, some mineral fertilizers (e.g., dusty single superphosphate) can stimulate the process of granulation of the organic-mineral fertilizing mixtures produced from municipal and industrial wastes.

While conducting the studies on the production of granulated organic-mineral fertilizers from municipal and industrial wastes, 45 fertilizing mixtures were created. These mixtures were then subjected to the process of granulation and the granulated organic-mineral fertilizers produced in such a way were tested in the physical, chemical and vegetation experiments using different plants (Krzywy et al. 2012) [18].

Later on, the theoretical assumptions of the granulated organic-mineral fertilizers production using municipal sewage sludge from the municipal sewage treatment plant in Stargard Szczeciński are presented (Tab. 1) (Krzywy et al. 2013) [19], and using ashes from brown coal originating from the heat and power plant Adamów (Krzywy et al. 2012, 2013) [18, 19].

The municipal sewage sludge contained 23.3% of dry matter, 445 g C organic·kg⁻¹d.m., 40.1 g N kg⁻¹d.m., 20.5 g P·kg⁻¹d.m. and 3.5 g K· kg⁻¹d.m. Ashes from brown coal did not contain organic C (organic matter) nor N. It was characterised by 98% content of dry matter and 24.8 g P· kg⁻¹d.m. and 5.76 g K· kg⁻¹d.m. (Krzywy et al. 2012, 2013) [18, 19].

Contamination with heavy metals of both wastes did not exceed the limits stated in the Regulation of the Minister of Environment (Journal of Laws, 10.137.924) and Regulation of the Minister of Agriculture and Rural Development (Journal of Laws, 08.119.765).

Considering the above-mentioned data and recommendations concerning the chemical composition of the fertilizing mixtures intended for granulation in order to receive granulated organic-mineral fertilizer, the percentage composition of the mixture calculated for the dry matter was established:

- 55% of municipal sewage sludge,
- 20% of ashes from brown coal,
- 12% of ammonium sulfate containing 20.5% of N,
- 4% of dusty single superphosphate containing 7% of P₂O₅ (7.42% P),
- 9% of potash salt containing 60% of K₂O (50% K).

Basing on the material and chemical composition of individual components, contents of macronutrients (N, P, K) were calculated for the fertilizing mixture intended for granulation (Tab. 6).

The data showed in the Table 6 indicate that the fertilizing mixture intended for granulation met the standards for the organic-mineral fertilizers concerning its chemical composition, and the N:P:K ration equalled to 1.0:0.41:1.03.

Upon the content of dry matter in the municipal sewage sludge (23.3%) and in the ashes from brown coal (98.0%), the amounts of fresh matter were calculated for the components that need to be used to prepare a batch of fertilizing mixture. The calculations show that to produce a batch of fresh matter of fertilizing mixture amounting to 281.2 kg, the following amounts need to be used:

- 236.0 kg of municipal sewage sludge,
- 20.2 kg of ashes from brown coal,
- 12.0 kg of 20.5% ammonium sulfate,
- 4.0 kg of 17% dusty single superphosphate,
- 9.0 kg of 60% potash salt.

Table 6

Percentage contents of organic carbon, organic matter, nitrogen, phosphorus, and potassium from individual components of the fertilizing mixture and their total contents in the mixture

Component	Components specification, kg d.m.				
	Organic C	Organic matter	Total N	Total phosphorus (P ₂ O ₅)	Total K (K ₂ O)
Municipal sewage sludge	24.47	41.6	2.20	1.12 (2.57)	0.20 (0.24)
Ashes from brown coal	none	none	none	0.50 (1.15)	0.11 (0.13)
Ammonium sulfate (20.5% N)	-	-	2.46	-	-
Dusty single superphosphate (17% P ₂ O ₅)	-	-	-	0.30 (0.68)	-
Potash salt (60% K ₂ O)	-	-	-	-	4.50 (5.42)
In total	24.47	41.6	4.66	1.92 (4.40)	4.81 (5.79)

Methods of Granulation of the Organic-Mineral Fertilizing Mixtures

In the preliminary stage of the study, attempts were made to granulate the obtained organic-mineral fertilizing mixtures. The components comprising the material composition of the fertilizing mixtures were mixed in such proportion to obtain 30 kg of each mixture. The components were mixed using a high-speed mechanical stirrer. The obtained mixtures were then conditioned for 14 days so the contained components would react and the dry matter content and the content of easily-assimilable macronutrients for plants would increase (decomposition of organic matter from the municipal sewage sludge). Then, the organic-mineral fertilizing mixtures were dried at temperature reaching 95°C. During drying the fertilizing mixtures mass transformed into a form of sinters of up to 6 cm. After drying, the organic-mineral fertilizing mixtures contained from 6 to 10% of humidity (90–94% d.m.). The obtained sinters were powdered. The fertilizing mixtures prepared in such a way with the addition of 2% to 5% (in relation to the mixtures

weight) of sodium lignosulfonate (factor stimulating the granulation) were granulated in the drum granulator. Sodium lignosulfonate was a very good factor stimulating the granulation of the organic-mineral fertilizing mixtures but using it considerable increased the costs of producing the granulated organic-mineral fertilizers. Costs of production of granulated organic-mineral fertilizers using the sodium lignosulfonate could not result in positive economic result. Therefore, for further studies different cheaper methods of the organic-mineral fertilizing mixtures granulation were used.

It is currently recommended to use binding agents enabling reaching required solidity of the obtained fertilizing granules. In production of granulated mineral fertilizers, bentonite binders are recommended. These binding agents assure the right solidity of created granules. Moreover, they have an ability of absorption of the fertilizing substances and their gradual release from the granules after applying into the soil. Using binders from the group of bentonites considerably increases the time of fertilizers exploitation and improves their effectiveness. The following bentonite binders need to be mentioned: bentolizer S, bentolizer SN, bentolizer S Extra, and bentolizer SN Extra. These are improved bentonites of high purity having very high binding ability. It is enough to add only a small amount of these binding agents to the fertilizer to ensure proper quality of granules.

Looking for cheap methods of granulation of the fertilizing mixtures, the possibility of using the extruded-expelled pulp was considered; the pulp was obtained from the Chemical Plant „Fosfan” S.A. in Szczecin producing compound mineral fertilizers and dextrans. The studies were conducted on the fertilizing mixture containing, calculated for dry matter: 40% of municipal sewage sludge, 40% of ashes from brown coal, 10% of dust single superphosphate (17.0% P₂O₅), 5% of ammonium sulfate (20.5% N), and 5.0% of potash salt (60% K₂O).

Table 7 presents chemical characteristics of components of the organic-mineral mixtures produced with the addition of the extruded-expelled pulp or dextrans.

Table 7

Chemical characteristics of components of the organic-mineral mixtures intended for granulation

Determined parameter	Component				
	municipal sewage sludge	ashes from brown coal	granulated single superphosphate	ammonium sulfate	60% potash salt
pH in H ₂ O	7.5	12.7	nd*	nd	nd
Dry matter, %	22.5	98.0	nd	nd	nd
Total content in g·kg ⁻¹ d.m.					
Organic C	422	none	nd	nd	nd
Nitrogen (N)	43.0	none	nd	205	nd
Phosphorus (P)	21.6	2.48	7.41**	nd	nd
Potassium (K)	5.10	5.76	nd	nd	500
Calcium (Ca)	24.5	225	nd	nd	nd
Magnesium (Mg)	2.90	12.0	nd	nd	nd
Sulfur (S)	5.95	2.95	116.0	nd	nd
Total content in mg·kg ⁻¹ d.m.					
Cadmium (Cd)	2.95	1.95	nd	nd	nd
Chromium (Cr)	56.0	12.5	nd	nd	nd
Copper (Cu)	120.0	25.6	nd	nd	nd
Nickel (Ni)	24.3	12.0	nd	nd	nd
Lead (Pb)	59.7	14.2	nd	nd	nd
Zinc (Zn)	1080	220.0	nd	nd	nd

Explanations: *nd – not determined, ** form of phosphorus soluble in mineral acids

The data (Tab. 7) indicate that the components intended for production of granulated organic-mineral fertilizers (municipal sewage sludge and ashes from brown coal) contained macronutrients

necessary for the growth and development of plants, and their contamination with heavy metals did not exceed the limits stated in the Regulation of the Minister of Environment (Journal of Laws 10.137.924) and Regulation of the Minister of Agriculture and Rural Development (Journal of Laws 08.119.765). Moreover, the $\text{pH}_{\text{H}_2\text{O}}$ value of the municipal sewage sludge ($\text{pH}_{\text{H}_2\text{O}}$ 7.5) and the ashes from brown coal ($\text{pH}_{\text{H}_2\text{O}}$ 12.7) indicate that granulated organic-mineral fertilizers with a share of these wastes can be used to deacidify the soil and improve other indicators of the soil fertility.

The produced organic-mineral fertilizing mixture was divided into three parts that were subjected to granulation using aiding agents – water and the extruded-expelled pulp obtained from the Chemical Plant „Fosfan” S.A. in Szczecin with the addition of 5% m/m of dextrin in relation to the fertilizing mixture weight.

Table 8 shows some physical parameters of the granulated organic-mineral fertilizers obtained with different agents aiding the process of granulation.

Table 8

Some physical parameters of granulated organic-mineral fertilizers produced from the fertilizing mixture containing municipal sewage sludge and ashes from brown coal using different agents aiding the process of granulation

Agents aiding the process of granulation		
water	extruded-expelled pulp	extruded-expelled pulp + 5% m/m dextrin
granulation		
Fairly good granulation. Light granules, easy to crush	Fairly good granulation. Light granules, easy to crush Lower amount of undersized grain. This increases the efficiency	Fairly good granulation. Light granules, adhering better. More big granules
after drying		
Hard granules, hard to crush	Very hard granules, hard to crush	The hardest granules, hard to crush

(source: Krzywy 2012 [18])

The results presented in the Table 8 indicate that granulated organic-mineral fertilizers of hard granules were obtained, especially after using addition of 5% m/m dextrin as the aiding agent.

Summary

The conducted studies proved that the discussed municipal and industrial wastes can be used to produce granulated organic-mineral fertilizers. This way it is possible to obtain cheap source of nutrients for plants, to improve the fertility of soils and decrease the amount of wastes in the environment which can sometimes lead to its contamination. The discussed wastes and fertilizers made out of them have to meet the requirements stated in the standards in relation to the contents of plant nutrients and a degree of their chemical contamination, and in the case of municipal sewage sludge, additionally, the contamination with pathogenic microbes of the alimentary track have to be controlled. These standards are contained in the Regulation of the Minister of Environment (Journal of Laws, 10.137.924) and Regulation of the Minister of Agriculture and Rural Development (Journal of Laws, 08.119.765). Therefore, every batch of wastes intended for production of granulated organic-mineral fertilizers should be subjected to adequate chemical and microbiological analyses.

While determining the material and chemical composition of the granulated organic-mineral fertilizers (formulas), the objective of their usage has to be indicated (soil fertilization and plant nutrition, soil recultivation etc.).

During production of organic-mineral fertilizing mixtures, and then, the granulated fertilizers, chemical changes and changes of their composition can occur. This mainly concerns organic matter and nitrogen. In relation to the above, each batch of produced fertilizers should be analysed chemically to determine its accurate composition.

Literature

1. Baran S.: *Osady ściekowe w gospodarce rolno-środowiskowej*. (Sewage sludge in agri-environmental management). Zesz. Prob. Post. Nauk Rol. 2004, **499**, 15–20.
2. Baran S., Wójcikowska-Kapusta A., Żukowska G.: *Wpływ osadu ściekowego i pożytkowej wełny mineralnej na zawartość próchnicy i form ołowiu w rekultywowanym utworze glebowym*. (Influence of the sewage sludge and extruded- expelled mineral wool on the content of humus and forms of lead in the recultivated soil). Zesz. Prob. Post. Nauk Rol. 2008, **533**, 31–38.
3. Berg W., Fenerborn H.: *Przetwarzanie i wykorzystanie popiołów wysokowapniowych. Popioły lotne z węgla brunatnego w Europie. Właściwości i zastosowanie*. (Processing and using the high-calcium ashes. Fly ashes from brown coal in Europe. Properties and application). Materiały z Międzynarodowego Seminarium Naukowo-Technicznego. Wyd. Ekotech, Bełchatów 2006, 19–25.
4. Bolt A., Byczkowski M.: *Zastosowanie popiołów do wzmacniania zdegradowanego podłoża gruntowego*. (Using ashes to reinforce the degraded ground). Materiały z IX Międzynarodowej Konferencji, Popioły z energetyki, Ustroń 2002, 313–325.
5. Czekala J.: *Właściwości chemiczne kompostu wytworzonego z komunalnego osadu ściekowego i różnych bioodpadów*. (Chemical properties of the compost obtained from the municipal sewage sludge and different biowastes). J. Res. Appl. Agric. Eng. 2008, **3**, 53, 35–41.
6. Dach J., Zbytek Z.: *Kompostowanie osadów ściekowych. Wpływ dodatku słomy*. (Composting the sewage sludge. Effect of adding straw). Przegląd Komunalny 2005, **5**, 43–45.
7. Drab M., Więcelewski S., Długosz A.: *Działanie nawozowe osadu ściekowego mechaniczno-biologicznej oczyszczalni miasta Zielona Góra*. (Fertilising action of the sewage sludge of the mechanical-biological treatment plant of the town of Zielona Góra). Zesz. Probl. Post. Nauk Rol. 2004, **499**, 69–78.
8. Galos K., Uliasz-Bocheńczyk A.: *Źródła i użytkowanie popiołów lotnych ze spalania węgla w Polsce*. (Sources and usage of fly ashes from combustion of coal in Poland). Gospodarka Surowcami Mineralnymi i Energią PAN 2005, **21**, 1, 24–35.
9. Gawlik L., Grudziński Z., Lorenz U.: *Wybrane problemy produkcji i wykorzystania węgla brunatnego*. (Chosen issues of production and usage of brown coal). Górnictwo i Geoinżynieria. Wyd. AGH, Kraków 2007, **31**, 2, 241–252.
10. Kaczor A., Kowalski G., Brodowska M.: *Zawartość i pobranie mikrośladników przez rzepak jary w warunkach stosowania osadu pościekowego i wapna poślotacyjnego*. (Content and assimilation of micronutrients by the spring rape under conditions of using sewage sludge and flotation lime). Zesz. Probl. Post. Nauk Rol. 2006, **512**, 239–246.
11. Kanafek J., Szczygielski T.: *Zarys wykorzystania popiołów wysokowapniowych w Polsce. Przetwarzanie i wykorzystanie popiołów wysokowapniowych*. (Outlines of using high-calcium ashes in Poland. Processing and usage of high-calcium ashes). Materiały Międzynarodowego Seminarium Naukowo-Technicznego. Wyd. Ekotech-Bełchatów 2006, 5–9.
12. Karoń B., Pietr S. J.: *Wartość nawozowa kompostu z osadu ściekowego*. (Fertilisation value of compost from sewage sludge). Zesz. Prob. Post. Nauk Rol. 2006, **512**, 305–313.
13. Klasa A., Czaplą J., Nogalska A.: *Komposty z odpadów organicznych jako źródło składników pokarmowych dla roślin warzywnych*. (Composts from organic wastes as a source of nutrients for vegetable plants). Zesz. Prob. Post. Nauk Rol. 2006, **512**, 323–337.
14. Kowalczyk-Juśko A.: *Popiół z różnych roślin energetycznych*. (Ash from different energy crops). Proceedings of ECOpole 2009, **1**, 3, 159–164.
15. Krzywy E., Wołoszyk Cz., Iżewska A.: *Wartość nawozowa komunalnych osadów ściekowych*. (Fertilisation value of municipal sewage sludge). PTIE Oddział Szczeciński 2000, 61.
16. Krzywy E.: *Żywnienie roślin*. (Plant nutrition). Wydaw. A R w Szczecinie 2007, 178.

17. Krzywy E., Krzywy-Gawrońska E., Iżewska A.: *Badania nad wykorzystaniem odpadów przemysłowych do produkcji nawozów organiczno-mineralnych oraz ich wpływ na żyzność i urodzajność gleb.* (Studies on using the industrial wastes to produce organic-mineral fertilization and their influence on fertility and fecundity of soils). Sprawozdanie końcowe z badań przeprowadzonych w ramach projektu badawczego MNiSW (End report on the studies performed within the research project of the Ministry of Science and Higher Education) NN 305 155 136, 2012, 70.
18. Krzywy E., Ciubak J., Cydzik E., Moździerz E., Kucharska M.: *Wykorzystanie komunalnych osadów ściekowych i popiołów z węgla brunatnego do produkcji granulatów nawozowych.* (Using municipal sewage sludge and ashes from brown coal to produce fertilizing granulates). *Chemik* 2012, **66**, 11, 1163–1168.
19. Krzywy E., Moździerz E., Wołoszyk Cz.: *Wykorzystanie odpadów przemysłowych do wytwarzania mieszanin nawozowych.* (Using industrial wastes to produce fertilizing mixtures). *Przemysł Chemiczny* 2013, **92**, 7, 1261–1263.
20. Krzywy E., Moździerz E.: *Wykorzystanie odpadów przemysłowych i komunalnego osadu ściekowego do produkcji granulatów nawozowych.* (Using industrial and municipal sewage sludge to produce fertilizing granulates). *Chemik* 2013, **67**, 7, 620–627.
21. Krzywy E., Moździerz E.: *Produkcja mieszanek nawozowych z udziałem odpadów przemysłowych oraz ich wpływ na wielkość plonów i zawartość makroskładników w roślinach testowych.* (Production of fertilizing mixtures using industrial wastes and their influence on the yield size and on the content of of macronutrients in the tested plants). *Przemysł Chemiczny* 2013, **92**, 8, 1538–1541.
22. Krzywy-Gawrońska E.: *Dynamika zmian właściwości fizyczno-chemicznych kompostów i ich wpływ na żyzność gleby oraz na wielkość i jakość plonu żyty trwałej.* (Dynamics of the physical-chemical properties of composts and their influence on the fertility of soil and on the amount and quality of yield of rye-grass). Rozprawa doktorska (Doctoral dissertation), AR w Szczecinie 2006, 138.
23. Ostrowski M.: *Charakterystyka morfologii popiołów lotnych ze spalania węgla brunatnych.* (Characterisation of morphology of the fly ashes from brown coal combustion). *Instytut Ceramiki i Materiałów Budowlanych, Warszawa-Opole* 2001, **8**, 136–150.
24. Palarski J., Pierzyna P., Strozik G.: *Zastosowanie ubocznych produktów spalania w technologiach górnictwa węgla kamiennego.* (Using combustion by-products in the technologies of hard coal mining). *Międzynarodowa Konferencja Eurocoalash* 2008, 315.
25. Piekarczyk M.: *Zawartość przyswajalnych form niektórych makro- i mikroelementów w glebie lekkiej nawożonej popiołem ze słomy pszenicy ozimej.* (Content of assimilable forms of some macro- and micronutrients in light soil fertilized with ashes from the winter wheat straw). *Fragm. Agron.* 2013, **1**, 30, 92–98.
26. Piekarczyk M., Kotwica K., Jaskulski D.: *Wpływ stosowania popiołu ze słomy jęczmienia jarego na chemiczne właściwości gleby lekkiej.* (Influence of using ashes from spring barley straw on the chemical properties of light soil). *Fragm. Agron.* 2011, **3**, 28, 91–99.
27. Rosik-Dulewska Cz.: *Fermentacja i kompostowanie odpadów organicznych. Twórczy ferment.* (Fermentation and composting organic matter. Creative ferment). *Recykling odpadów* 2008, **16**, 4, 4–7.
28. Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi w sprawie wykonywania niektórych przepisów ustawy o nawozach i nawożeniu (Regulation of the Minister of Agriculture and Rural Development on execution of some regulations of the act on fertilizers and fertilization) (Dz. U. 08.11.97.65).
29. Rozporządzenie Ministra Środowiska w sprawie komunalnych osadów ściekowych (Regulation of the Minister of Environment on municipal sewage sludge) (Dz. U. 10.137.924).
30. Sikorski M., Matyja J.: *Kompostowanie osadów ściekowych z odpadami roślinnymi.* (Composting sewage sludge with vegetable wastes). *Zesz. Prob. Post. Nauk Rol.* 2008, **526**, 437–442.
31. Skalmowski K.: *Przewodnik gospodarowania odpadami.* (Guide to managing wastes). *Wyd. Verlag Dashofer* 1999, cz. 4, rozdz. 4, podroz. 1.6, 1–28.
32. Stankowski S., Krzywy E.: *Zawartość głównych składników pokarmowych dla roślin i metali ciężkich w nadkładach i podkładach modelu rekultywacyjnego składającego się z popiołu z węgla kamiennego oraz komunalnych osadów ściekowych.* (Content of main plant nutrients and heavy metals in the overlay and underlay of the recultivation model comprising of ashes from hard coal and municipal sewage sludge). *Zesz. Prob. Post. Nauk Rol.* 2004, **499**, 315–323.
33. Stolecki L.: *Wpływ sposobów składowania odpadów paleniskowych w wyrobisku końcowym odkrywką Belchatów na środowisko wodne.* (Influence of the manner of storing the combustion wastes in the end working of the open pit Belchatów on the water environment). *Rozprawa doktorska (Doctoral dissertation), Politechnika Wroclawska* 2005, 2–29.
34. Wysokiński A., Kalembsa S.: *Wybrane parametry fizyczno-chemiczne świeżych i kompostowanych osadów ściekowych oraz ich mieszanin z CaO lub popiołem z węgla brunatnego.* (Selected physical-chemical parameters of fresh and composted sewage sludge and their mixtures with CaO or ashes from brown coal). *Acta Sci. Pol. Form. Circ.* 2006, **1**, 5, 51–61.
35. Wysokiński A., Kalembsa S.: *Wpływ kompostów i osadów ściekowych z tlenkiem wapnia i popiołem z węgla brunatnego na zawartość wapnia i magnezu w roślinach.* (Influence of composts and sewage sludges with calcium oxide and ashes from brown coal on the content of calcium and magnesium in plants). *Zesz. Prob. Post. Nauk Rol.* 2009, **512**, 669–677.
36. Frankenstein K.: *Studia nad nawozowym wykorzystaniem kompostów z komunalnego osadu ściekowego.* *Rozprawa doktorska AR w Szczecinie* 115, 2002.
37. Stachyra K.: *Technologia przetwarzania możliwości zagospodarowania oraz ocena składu fizyczno-chemicznego powstałych osadów ściekowych oraz wyprodukowanego z ich udziałem kompostu w Komunalnej Oczyszczalni Ścieków w Słupsku.* *Praca magisterska*, 2012.
38. Goch J.: *Gospodarka ściekowo-osadowa na przykładzie Komunalnej Oczyszczalni Ścieków w Gryficach.* *Praca magisterska*, 2011.
39. Krzywy E., Krzywy J.: *Optymalizacja właściwości nawozowych odpadów pochodzenia organicznego w wyniku ich kompostowania. Wybrane aspekty zagospodarowania odpadów organicznych a produkcja biomasy wierzby energetycznej.* *Wyd. URzeszow, Rzeszów*, 2005, 41–62.
40. Drab M., Więcelewski S., Długosz A.: *Działanie nawozowe osadu ściekowego mechaniczno-biologicznej oczyszczalni miasta Zielona Góra.* *Zesz. Prob. Post. Nauk Rol.* 2004, **499**, 69–78.

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