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Recovery of phosphorus compounds from thermally-processed wastes

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Abstract. Depletion of phosphorus deposits is one of the most serious global problems, which may soon lead to a crisis in food production. It is estimated that if the current living standard is maintained, the available reserves will be depleted in 130 years. Considering the principle of sustainable development, searching for alternative phosphorus sources is extremely important. The work presented the results of the research on the possibility of utilizing wastes as a source of phosphorus. The studies were conducted on poultry manure. The physicochemical properties of phosporus-rich wastes were determined as well. The fertilizing properties of ashes from poultry manure combustion – obtained from different systems, i.e. caged and barn production. The assimilability of phosphorus from the obtained ashes was determined. Potential applications of phosphorus-rich ashes were proposed as well.

1. Introduction

Constantly increasing world population, industrial development, and the amount of migrating chemical substances in the environment contribute to both local and global changes [1]. Therefore, the world may soon face the problems of overpopulation, drinking water shortage, as well as deficit of energy and natural resources. Further development of civilization will depend on the possibility of restoring the balance between the economic development and the protection of natural resources [2], [3].

For many decades, the production processes were carried out without consideration for their impact on the natural environment. This resulted in the destruction of the environment, which enforced a change in the approach towards the issues of environmental protection. The actions involving the control of pollutants discharged from the industry, including wastewater treatment plant, disposal of waste and treatment of emitted gases, enabled to mitigate the degradation of environment. However, this strategy proved to be insufficient. Limiting the availability of non-renewable energy resources became the reason for changing the environmental protection strategy and the development of cleaner methods of production.

In accordance with the principles of cleaner production, wastes should be treated as a source of raw materials for the manufacturing of new, complete products. Examples include municipal sewage sludge and livestock production wastes [4].

Phosphorus is an element of great biological significance. Due to the minimal volatility and low solubility of phosphorus compounds, its availability for the living organisms is limited [1], [5]. Phosphorus is a structural element of plants as well as all living tissues and a nutrient for all organisms [6]-[9]. The growing population, and thus the increasing food production, results in a rising demand for phosphorus fertilizers and fodder additions.

In the developed countries, the phosphorus fertilizers constitute the greatest share as far as the use of phosphorus compounds is concerned. Combined with food and fodder additions, they account for 85% of total consumption. The remaining groups include detergents, constituting 12% and preparations for phosphate conversion coating and rust protection [10], [11].

The constantly growing demand for phosphorus compounds contributes to the exploitation of natural deposits of apatites and phosphorites. The volcanic deposits containing approximately 13% phosphorus, mainly composed of fluorapatite as well as the sedimentary deposits with about 87% phosphorus, predominantly comprising francolite, are economically important.

From the geological point of view, phosphorus is abundant; however, its usefulness is determined by the cost of extraction and processing of phosphate ore. The forecasts prepared at the end of the previous century indicate that over 50% of the currently exploited phosphorus resources will be depleted in the next 60-70 years. This tendency will surely contribute to a hike in the market price of this resource. Considering the current tendencies of phosphorus use, it may be estimated that the known reserves of this resource will be depleted in 130 years.

Taking into account the principles of sustainable development, alternative sources of phosphorus should be sought. This especially pertains to the possibility of its recovery and recycling from wastes, the most important of which include the recovery of phosphorus from municipal and industrial wastewater, sewage sludge and the use of phosphorus from poultry manure.

The aim of this work is to determine the possibility of utilizing ash from manure combustion as a potential source of phosphorus.

2. Materials and methods

2.1. Materials

Investigation of the poultry manure obtained from the caged and barn production systems was conducted for two series.

The employed production system has a significant impact on the quality, composition and properties of manure. The manure utilized in the studies originated from industrial poultry farms located in the Lubelskie voivodeship. The manure from the caged and barn production systems were investigated in the research. The composition of poultry manure is dependent on numerous factors, including bird's age, weight, fodder type and the amount of supplied water. This residue mainly comprises bird's droppings, feathers and scattered fodder. Two types of production systems were utilized in the study:

- caged production system, in which poultry is kept in cages individually supplied with fodder and water,
- barn production system, in which the birds are kept on litter in pens.

The caged production system restricts the movement of birds; hence, the consumption of fodder is reduced by 10-15% in comparison to the free range system.

2.2. Methods

In order to indicate the main and trace components in the considered materials, it was necessary to transform them into liquid form through mineralization with concentrated nitric acid.

The scope and analytic methods employed in the study:

- dry mass content in the wastes was determined with the gravimetric method. Drying of wastes was conducted by means of KC-65-M laboratory dryer at 105^0C (379K),
- heat of combustion and calorific values of sewage sludge were measured in accordance with the Polish PN-81/G-04513 standard. The studies involved the use of KL-11 colorimeter manufactured by Miakdo,

- sewage sludge was incinerated in SM-046 muffle furnace produced by Czylok-Sel (Figure 1) in 600 and 750^{0}C. The pre-dried poultry manure samples were subjected to incineration,
- mineralization with nitric acid was conducted in Multiwave 3000 manufactured by Anton Paar,
- the elemental composition of poultry manure ashes was indicated by means of ICP-EOS manufactured by JOBIN YVON,
- the content of calcium in manure was indicated by means of complexometric titration with sodium hydroxide,
- the contents and phosphorus and the phosphorus dissolved in citric acid were studied in accordance with the standard for conducting investigations on fertilizers.

Figure 1. Muffle furnace produced by Czylok-Sel

3. Results and discussion

The collected manure was dried until dry mass was obtained. The moisture content in manure amounted to 53-55% for caged poultry and 52-61% for the poultry farmed in barn production system. The dried manure was ground and divided into two parts; the calorific value was determined for one part, whereas the other was combusted.

The mean calorific value of manure amounted to 10 000 kJ/kg for poultry farmed without litter and 12 500 kJ/kg for the poultry farmed with litter. The obtained results for poultry manure from the barn production system exhibited the calorific value which was 2500 kJ/kg higher. This difference was caused by an additional straw content in the manure. Manure was combusted in 600 and 750 ℃. The mass loss for manure I and II reached 58.2% and 67.4%, respectively, mainly connected with the loss of organic mass. The conducted chemical analyses on the phosphorus and calcium content in the ash from the combustion of poultry manure from caged and barn production systems were included in Table 1.

While analysing the data from Table 1, a slight increase in the percentage of total P_2O_5 and P_2O_5 dissolved in citric acid was observed for the production system with litter, as well as a slight drop in the percentage of calcium.

Table 1. Composition of poultry manure from caged and barn production systems in air-dried state.

Component	Manure I	Manure II	Manure I	Manure II
	Without litter		With litter	
Total P_2O_5 [%]	4.8	5.1	5.4	6.1
P_2O_5 dissolved in 2% citric acid [%]	1.9	2.4	3.3	4.1
Ca%	15.8	10.9	8.6	10.9

Table 2. Composition of ashes from the combustion of poultry manure from caged and barn production systems.

Ash		P_2O_5 content (%)	Ca content (%)
		Caged production system	
Manure I	600 ℃	12.2	32.5
	750 ℃	13.1	38.4
Manure II	600 ℃	12.5	34.2
	750 ℃	13.6	40.9
		Barn production system	
Manure I	600 ℃	8.5	29.3
	750 ℃	12,1	25.1
Manure II	600 ℃	12.5	36.3
	750 ℃	14.2	41.1

Table 2 contains the results of determining the composition of ash from the combustion of poultry manure depending on the combustion temperature and production system. The analyses found in the table indicate a slight but clear increasing tendency within a given type of manure, regardless of production system. The same tendency is exhibited by the calcium percentage.
The conducted analyses of ash from the calcination of the manure ash from the caged and barn production systems indicate an increase in the content of certain analyzed elements, i.e. As, Cd, and Ni. In the case of As, a significant increase in the concentration was noted from 4.2 ppm (caged production system) to 682 ppm (barn production system), Cd: 0.72 ppm (caged production system) to 382 pp, (barn production system) and Ni: in over twice as high concentration than in the case of the caged production system (Table 3). It may be purported that large differences in the concentration of As, Cd, and Ni in the case of the barn production system stem from the application of straw, which increased the concentration of the enumerated metals. The type of utilized feed is irrelevant, because all the birds were fed with the same type of fodder. Slight differences could only result from the varying batch number.

Table 3. Ash composition obtained from the calcination of manure I ash from the caged and barn production systems at 600 °C.

Element	Unit	Concentration	
		Caged production system	Barn production system
Al	%	0.41	0,31
As	ppm	4.2	682
B	ppm	102	95
Ba	ppm	76	74
Cd	ppm	0.72	382
Cr	ppm	25	33
Cu	ppm	231	241
Fe	%	0.48	0.53
Hg	ppb	2.21	7

K	%	4.5	4.4
Mg	%	1.3	1.4
Na	%	0.5	0.88
Ni	ppm	43	109
Pb	ppm	-	-
Sr	ppm	326	332
Zn	%	0.115	0.11

However, the chemical analysis of litter and utilized feed were not studied, due to the unavailability of data.

The analysis of data in Figure 2 indicates that along with the rising calcination temperature of poultry manure ash from caged production system, a decrease in the ash assimilability occurs. It should also be noted that it is much lower than in the case of ash subjected exclusively to drying.

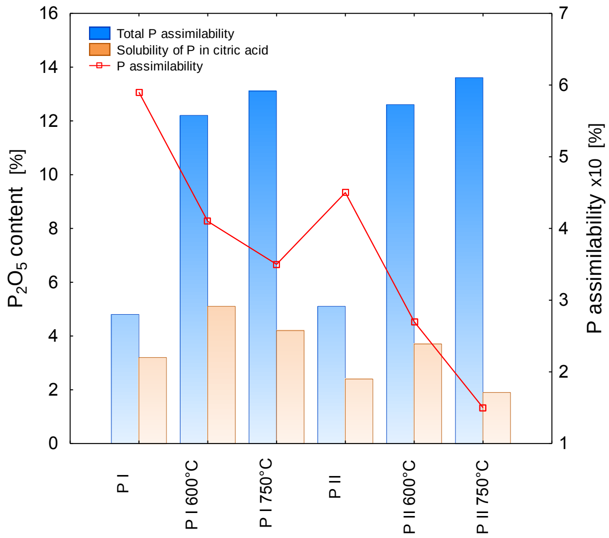

Figure 2. Impact of calcination temperature of poultry manure ash from caged production system on the total content and assimilability of phosphorus.

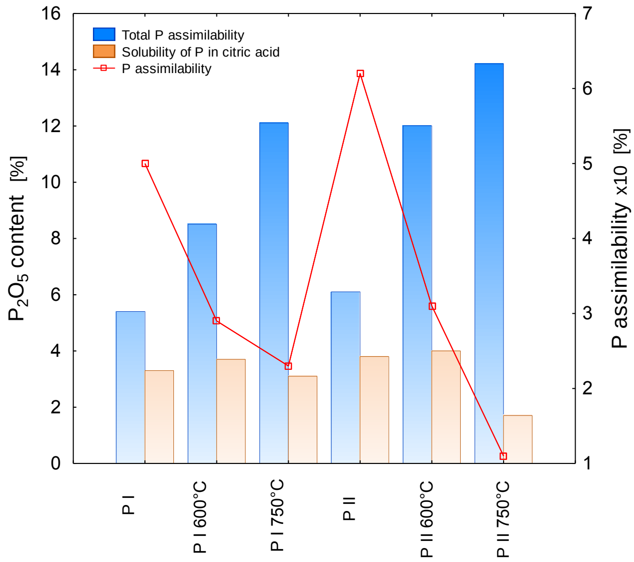

Figure 3. Impact of calcination temperature of poultry manure ash from barn production system on the total content and assimilability of phosphorus.

A similar tendency is exhibited by the poultry manure ash from barn production system. Its assimilability is much lower than in the dried manure (Figure3).

Similar analysis results were obtained by Wzorek [12], both in the case of the system with and without litter.

Therefore, direct use of non-processed poultry manure should also be considered due to the introduction of nitrogen and organic elements into soil, which are lost in the course of high-temperature processes. Therefore, the direct application of manure as a fertilizer seems preferable to their reduction to ashes.

Reduction of ash mass in relation to the original amount of manure, possibility of energy production from its combustion and removal of pathogenic organisms constitute the advantages of thermal processing.

4. Conclusion

Thus far, studies focused on the acquisition of phosphorus from the municipal and animal sewage. The conducted research showed that poultry manure may constitute a compost component, which provides valuable mineral and organic elements to soil, mainly nitrogen and calcium, as well as phosphorus, the primary sources of which are rapidly being depleted.

Management of manure is also connected with certain odour nuisance. It should be remembered that it may contain pharmaceutical drugs employed in industrial poultry farms and thus constitute a biological threat. Therefore, thermal utilization should be considered. Combustion of waste ensures a reduction in its mass by approximately 80%. High temperature eliminates all biological threats and odour nuisance.

As shown in the research, the temperature required for elimination of the organic fraction does not exceed 600 ℃. The obtained ashes are characterized by a low content of phosphorus, slightly exceeding 14% P_2O_5 which can subsequently be used as a fertilizer. The assimilability of phosphorus from ashes is much lower than in the case of dried manure.

Poultry manure should not be incinerated on their own due to high calcium content in relation to phosphorus. Co-incineration of poultry manure with other types of waste, e.g. sewage sludge, which also contain substantial amounts of phosphorus, appears to be advantageous. The resultant product may serve as a source of phosphorus for the chemical industry.

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