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ORIGINAL RESEARCH

Optimization of chicken manure combustion parameters in the aspect of phosphorus recovery

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Abstract

Purpose The increasing demand for phosphorus for the production of mineral fertilizers forces the continuous development of research and new technologies in the field of obtaining it from sources other than phosphate rocks. This paper presents an analysis of optimizing the combustion parameters of chicken manure in the aspect of phosphorus recovery.

Methods The combustion process was carried out in different time (3-8 hours) and temperatures (700-900 ºC) in laboratory of electric furnace. The content of macro and micronutrients was determined by XRF and ICP-OES analysis. To identify the mineral composition of ashes, the XRD analysis was applied. The content of total phosphorus in ash extracts was determined by photometric method.

Results Concentration of P_2O_5 in ash samples detected by ICP-OES and XRF was comparable, 30.37 wt.% and 31.77 wt.% at 900 ºC, 26.27 wt.% and 26.71 wt.% at 700 ºC and 25.31 wt.% and 25.00 wt.% at 500 ºC, respectively. The mineral composition of ashes showed two phases: crystalline and amorphous. The estimated values of P_2O_5 content in crystalline phase was 14.83 wt.% at 500 ºC, 20.96 wt.% at 700 ºC and 23.80 wt.% at 900 ºC. The estimated P_2O_5 content in amorphous phase was 10.48 wt.% at 500ºC and decreased at higher temperature to 5.31 wt.% at 700 ºC and 6.57 wt.% at 900 ºC.

Conclusion The chemical composition of ashes from chicken manure depends on the combustion temperature. The highest concentration of phosphorus in their bioavailable forms was determined for samples burned in 500 ºC. The results indicate that a valuable source of phosphorus is the amorphous phase.

Keywords phosphorus availability, Organic wastes, Ash, Amorphous phase

Introduction

Phosphorus is a key ingredient in fertilizers and an essential biological element for the proper development of plants. Almost 90% of this building material comes from non-renewable natural resources occurring in the form of phosphate rock. Due to the high demand for mineral fertilizer production, the consumption of natural phosphate deposits is constantly increasing, while their reconstruction takes from 10 to 15 million years (Gilbert 2009). Poland is among the world's top five consumers of elemental phosphorus at international market. In 2016, the consumption of this element in Poland amounted to 14%, which makes it the third next to Germany (20%), India (20%), Japan (13%) and Brazil (10%) (Othake and Tsuneda 2019).

It is estimated that 80-90% of the global demand for phosphorus is intended for the production of phosphoric acids for the formation of granular and liquid mineral fertilizers but also animal feed and supplements (Correll 1998; Jasinski 2019). According to the calculations, 75% of the world's phosphate resources are obtained from sedimentary and marine phosphate rock deposits (Van Straaten 2002). The best raw materials for the production of fertilizers are found among minerals of volcanic origin - apatites, whose general formula is $Ca_{10}(PO_4)_6(X)_2$, where X is F^-, OH^- or Cl^- or carbonate (Elliott 1994), as well as minerals of sedimentary origin - phosphates. Compared with apatites, phosphates contain higher amount of carbonates, organic compounds and radioactive substances. The production of agricultural fertilizers from phosphate rock is also hindered by its inherent admixtures of iron, aluminium and heavy metals (Łuczkowska et al. 2016). Nevertheless, the phosphate rock is more significant in economic terms as its deposits outweigh the number of available apatite deposits.

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The world's largest phosphate-rock reserves are located in Russia, the USA (Florida and North Carolina), China and north African countries (Jasinski 2019). European countries are entirely dependent on the import of phosphorus in its natural form. The state of the world's phosphate rock resources in Europe is estimated at slightly above 1% (Samreen and Kausar 2016).

Phosphate ores are divided into three categories of raw materials according to the content of phosphorus pentoxide (P_2O_5), namely: low-grade phosphate (12-16%), moderately low-grade phosphate (17-25%) and high-grade phosphate (26-35%). Deposits with P2O5 content in the final product above 28% are considered economically viable (Sengul et al. 2006; Samreen and Kausar 2016).

Pure fluor-apatite may contain up to 42% P_2O_5, and the carbonate-substituted form of apatite up to 34% P_2O_5 (Van Vuuren et al. 2010). Assuming a steady increase in the phosphorus demand for mineral fertilizer production by 1.5% per year (Steen 1998), it is anticipated that natural phosphorus deposits will have been depleted within the next 60-90 years (Reinhard et al. 2017; Van Vuuren et al. 2010; Li et al. 2019). For this reason, intensive research is being carried out around the world to recover phosphorus from waste, i.e. sewage sludge or animal manure, which are a valuable source of this element and can offer an alternative to the technology of obtaining it from natural phosphate rocks (Wzorek et al. 2008; Ciesielczuk et al. 2016; Havukainen et al. 2016). According to scientific literature data, currently only 1-2% of phosphorus is recovered from biogenic resources, i.e. bird and bat excrements (Van Straaten 2002).

For a long time, a significant increase in poultry farming has been observed in the world. According to data from 2000-2017 in Poland, there was a threefold increase in chicken poultry production, which accounts for over 90% of total poultry (48.3 million to 176.7 million units, respectively) (Statistics Poland 2017). Given that the amount of litter from one bird amounts to approx.100 g/day (Myszograj and Puchalska 2012), it is estimated that 12.4 million tons of fresh chicken manure is generated weekly, which must be properly utilized. Traditionally, chicken manure is used in agriculture as fertilizer for vegetable crops. Since it contains large amounts of protein, fibre and minerals, it has also been used as an additive in feed for ruminants (Baki Unal et al. 2015). Unfortunately, in addition to nutrients, the chicken manure also includes contaminants in the form of toxic metals and pathogenic microorganisms (Bicudo and Goyal 2003; Chen and Jiang 2014), which pose a serious threat to human health and aquatic ecosystems. Closed poultry production systems also require the use of appropriate feed additives in the form of antibiotics, arsenic and coccidiostats, which are excreted from the digestive system along with faeces (Bolan et al. 2010). In addition, as noted above, feed additives such as antibiotics, arsenicals, and coccidiostats are added in poultry diet, which can be excreted as waste by-products.

For this reason, a constant development of poultry manure processing technology is being observed worldwide, its purpose being not only its safe utilization but also the recovery of valuable nutrients, i.e. phosphorus, nitrogen, potassium.

In recent years, a lot of attention has been focused on the use of animal biowaste in the anaerobic digestion process for biogas production (Pavlostathis and Giraldo-Gomez 1991; Wu et al. 2019). The processes of pyrolysis and combustion of manure to obtain heat energy are areas of even greater interest (Kelleher et al. 2002).

Current technologies used in the phosphorus recovery process as a result of burning poultry manure have proved to be economically unviable. Another problem is the quality of the concentrate obtained as a result of phosphorus extraction, i.e. the concentration of the desired element and the presence of impurities in the form of unburned coal and silica glaze. The latest research has shown that the amorphous phase is the source of the bioavailable form of phosphorus contained in poultry ashes. Experiments on poultry manure samples combustion for 2 hours at 500, 750 and 1000 °C have shown that the proportion of amorphous phase in ashes is significant and depends on the combustion temperature of the sample (Vance 2019). This paper presents the results of research on ashes obtained in the process of chicken manure combustion, depending on the time and temperature process parameters applied. The analysis was aimed at optimizing the combustion process in terms of the availability of phosphorus in the crystalline and amorphous phases and its recovery in future research stages.

Materials and methods

Materials

Samples of fresh chicken manure were taken during winter time from the Polish egg laying hens farm in the Silesian region. During the research period, the flock had 52,000 birds not older than 16 weeks. The average laboratory sample weighing 1 kg was transported to the laboratory, dried to the analytical state at 40 °C for 2 days, milled to a grain diameter of max. 200 µm and marked with the symbol K0.

The chicken feed supplement (Cargill Poland) composed of 0.60 wt.% phosphorus, 0.77 wt.% calcium, 0.15 wt.% sodium, trace amounts of iron, selenium, copper, manganese, zinc, iodine and other ingredients such as vitamins and additives.

The combustion process was carried out using the NABERTHERM high temperature chamber furnace

HT 16/16 with a P310 controller. The furnace had a heating chamber with a capacity of 16 litres and the ability of continuous operation at temperatures up to 1600 °C. Samples were burned at 500, 700 and 900 °C with a heating rate of 10 °C/min for 3, 5 and 8 hours, respectively. The manure sample was placed in the chamber in the amount of 10g in a corundum crucible. Before burning, the sample was heated for 30 minutes at 140 °C to completely remove residual moisture. A list of sample symbols K1-K9 along with the combustion process parameters are given in Table 1.

Table 1 List of tasted samples

Parameters of combustion process	Sample									
	K0	K1	K2	K3	K4	K5	K6	K7	K8	K9
Temperature, °C	Input	900	700	500	900	700	500	900	700	500
Time, h		5	5	5	3	3	3	8	8	8

Methods

The moisture content of sample K0 was determined by the gravimetric method by drying to constant weight at 105 °C. Loss-on ignition (LOI) was determined by burning the sample in a muffle furnace at 950 °C. The total content of macroelements and trace elements in the raw sample K0 and in post-combustion samples K1-K9 was determined by means of wavelength-dispersive X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES). The X-ray powder diffraction (XRD) was used to identify crystalline and amorphous phases contained in the ash samples.

The content of total phosphorus in the water extracts from ash samples and in the extracts from calcium lactate solution was determined by photometric method.

XRF analysis

X-ray measurements were performed by spectrometer Rigaku ZSX Primus with a rhodium target X-ray tube (max. power 4 kW). The research was performed with the application of fine collimator, analysing crystal LiF200 and a scintillation counter as a detector. The X-ray tube was operated at 50 kV and 60 mA. The measurements were performed in a vacuum. The time of the analytical line measurement was 60 s, whereas the time of background measurement was 30 s.

ICP-OES analysis

Perkin Elmer Optima 5300 ICP-OES analyser was used to determine the elemental composition of the sample K0, i.e.: C, N, Ca, K, P, Mg, Cl, S, Si, Fe, Al, Zn, Mn, Ba, Pd, Cs, Ti, Cu, Sr, Ni, Rb. The analysis was performed after mineralization of the material in a mixture of HCl and HNO_3 acids (3:1 ratio).

The ICP-OES method was also used to determinate the concentration of P_2O_5 in sample K1, K2 and K3.

XRD analysis

Phase identification was performed using powder X-ray diffusion (DSH) in Bragg-Brentano geometry, using a Bruker D8 DISCOVER diffractometer, CuKα radiation, Ni filter and LYNXEYE_XE detector. Mineral composition was determined and calculated on the basis of standards licensed in PDF-4 + 2019 RDB ICDD (International Centre for Diffraction Data) and databases: ICSD (Inorganic Crystal Structure Database) and NIST (National Institute of Standard and Technology). DIFFRAC v.4.2 and TOPAS v.4.2, Bruker AXS programmes were applied for registration and diagnostics.

Extraction and photometer analysis

A weighted amount of 1 g ash was placed in a 100 cm^3 cylinder, followed by the addition of 50 cm^3 0.04M calcium lactate with pH 3.6. At the same time, water extracts from aqueous solutions were made by mixing 1g of ash with 10 cm^3 of distilled water. The samples were centrifuged on a rotary mixer at a speed of 40 rpm for a period of 8 hours for aqueous solutions and 1.5 hours for calcium lactate solutions. The samples were then centrifuged for 10 min (Eppendorf 5810) and filtered using Whatman filters pore size 45 µm to obtain a clear solution. Total phosphorus content was determined by photometric method using Nanocolor phosphorus total 1 (0.01-1.5 mg/l P), total 5 (0.2-5 mg/l P), and total 45 (5.0-50) test tubes using a Nanocolor 500D photometer (Macherey-Nagel GmbH & Co. KG, Germany).

Results and discussion

Characteristics of dried chicken manure

According to the scientific literature review, the chemical composition of the tested material and dry matter (DM) content (Table 2) were similar to the results described by the authors of another paper (Kucharski and

Białecka 2019). The phosphorus content in poultry manure varies considerably with the kind of animal, feeding, the type of supplementary materials and husbandry practices (Yokota et al. 2003). According to research conducted by a number of authors and developed by Othake and Tsuneda 2019, the vast majority of phosphorus occurs in inorganic form, i.e. 32-84 wt.%. The content of phosphorus in organic form is in the range of 14-68 wt.%, the remaining part being its residual form at 0-24 wt.%.

Among the biophilic elements in plant development, i.e. nitrogen, phosphorus and potassium, their content in the sample mass was: 5.67, 2.01 and 2.36 wt.%. The ratio of carbon content to total nitrogen (C:N) was above 7:1, and the ratio of nitrogen to phosphorus (N:P) was approximately 3:1. The sample also contained 2.4 wt.% of calcium, while the content of other components, i.e. magnesium, aluminium, silicon and sulphur, did not exceed 1 wt.%. The presence of calcium and magnesium in fertilizers has a deacidifying effect on the soil and positively affects plant development.

Table 2 Result of the chemical characterization of chicken manure - K0

Element	wt.% (DM)	Element	ppm (DM)
O	42.35	Cs	200
C	41.85	Fe	780
N	5.67	Al	500
Ca	2.40	Zn	430
K	2.36	Mn	380
P	2.01	Ba	370
Cl	0.87	Sr	30
Mg	0.85	Ti	90
Na	0.53	Cu	70
Pd	0.02	Ni	20
S	0.62	Rb	10
Si	0.18	others	10

The metals detected in the tested sample stem from the feeds used for the birds bred in closed production systems. The addition of metals to nutritional supplements in farmed poultry is aimed at accelerating the growth of broiler body weight and increasing the productivity of laying hens, as well as preventing the formation of disease outbreaks. The content of some metals in soil, i.e. Cu, Zn, Ni, Mn, has a positive effect on plant development; however, their excessive amount in fertilizers can be toxic. According to the Polish regulations (Minister of Agriculture and Rural Development 2008), the permissible content of pollutants in organic and organic-mineral fertilizers must not exceed ppm (DM): 140 Pb, 100 Cr, 60 Ni, 5 Cd and 2 Hg.

Chemical properties of ashes

Test results indicate that the increase in temperature and longer combustion time favoured an increase in sample weight loss, which resulted in reduced ash yield (Fig. 1). The reduction of ash yield obtained during the combustion of various animal specimen samples (cattle, layer and swine manure) at temperatures of 400-900 °C was previously described in studies conducted by Huang et al. (2011). As shown in Table 3, the obtained loss-on ignition (LOI) value for samples burned at 500 °C ranged from 16.99 wt.% (3h) up to 12.68 wt.% (8h), while at higher temperatures, i.e. 700 °C and 900 °C, the determined range of LOI was 10.38-8.35 wt.% and 1.73-0.21 wt.%, respectively.

Moreover, the analysis showed that the combustion time of manure samples did not significantly affect the chemical composition of ashes (Table 3). The obtained contents of chemical components were comparable and were within the error limit of ± 1 wt.%, however a slight increase at higher combustion temperature was noted. The average content of P_2O_5 at 500 °C was 25.02 wt.% and 33.24 wt.% at 900 °C. A visible increase in the content of the component depending on the temperature was also obtained for CaO (19.56 and 26.16 wt.%), MgO (6.34 and 8.64 wt.%); Al_2O_3 (0.74 and 0.98 wt.%) and Fe_2O_3 (0.75 and 1.03 wt.%) at 500 °C and 900 °C, respectively. In the case of Na_2O and Si_2O, the increase in these values was not significant, while a decrease in the amount of this component was observed for K_2O from 16.42 wt.% at 500 °C to 14.20 wt.% at 900 °C. Small amounts of Mn_3O_4, ZnO and TiO_2 were also determined in the samples of the concentrations not exceeding 0.5 wt.%. In addition, chlorine was identified, the amount of which decreased as the combustion temperature increased, reaching a concentration of 5.05 wt.% at 500 °C, 4.57 wt.% at 700 °C and 0.62 wt.% at 900 °C.

In order to verify the results obtained from XRF analysis, the content of P_2O_5 in ash samples (K1, K2 and K3) was determined also by using ICP-OES method. The result of experimental data shown in Fig. 2 indicates similar values of the P_2O_5 content in ICP-OES with XRF analysis, 30.37 wt.% and 31.77 wt.% at 900 °C (K1), 26.27 wt.% and 26.71 wt.% at 700 °C (K2) and 25.31 wt.% and 25.00 wt.% at 500 °C (K3), respectively. A low measurement error was obtained and the difference between the results from ICP-OES and XRF analysis did not exceed 1.4%.

Combustion of a mixture of broiler and laying hen manure was the subject of intensive research conducted in the Netherlands (Kema Milieu Technology) and Great Britain (Fibrowatt). The percentage yield of P_2O_5 in ashes obtained from these raw materials was 24 and 21 wt.%, respectively (Van Voorneburg et al. 1998). A high value of phosphorus total amounting to approximately 110 g/kg (25 wt.% P_2O_5) was also found in the

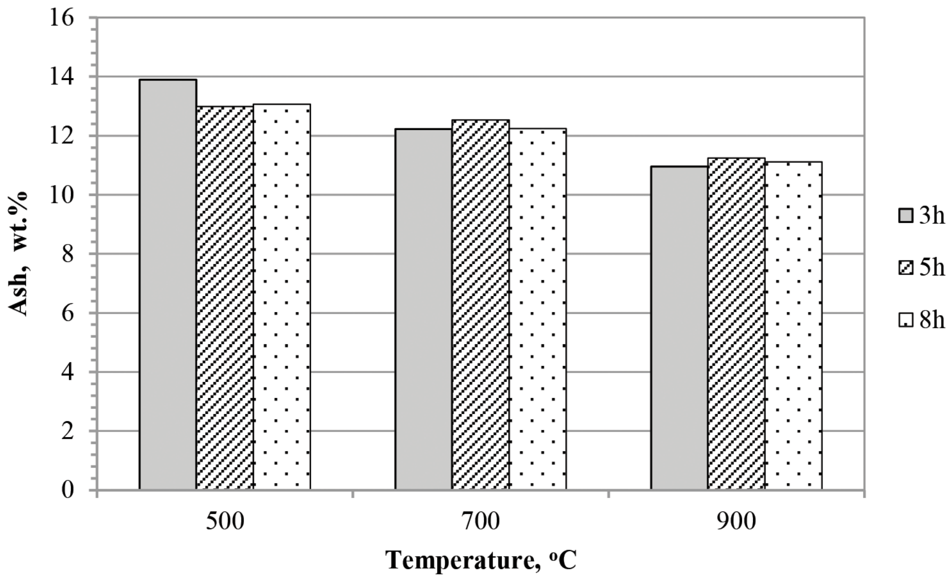

Fig. 1 Efficiency of chicken manure ash depending on the time and temperature of combustion

Table 3 Chemical composition of ash (wt.%) depending on the time and temperature of combustion using XRF method

Parameter	Ash sample								
	K1	K2	K3	K4	K5	K6	K7	K8	K9
T(°C)/time (h)	900/5	700/5	500/5	900/3	700/3	500/3	900/8	700/8	500/8
SiO_2	4.76	3.08	2.69	3.72	3.19	3.23	3.84	2.90	3.17
Al_2O_3	0.90	0.86	0.69	0.99	0.82	0.78	1.04	0.74	0.74
Fe_3O_4	0.97	0.83	0.72	1.05	0.85	0.79	1.07	0.78	0.74
CaO	27.33	21.57	19.49	25.32	20.71	19.46	25.83	19.43	19.74
MgO	8.44	7.02	6.52	8.69	6.72	6.05	8.78	6.48	6.46
Na_2O	4.13	3.72	3.66	3.90	3.58	3.24	4.19	3.55	3.55
K_2O	13.79	16.86	16.72	14.46	16.65	15.83	14.36	16.39	16.73
SO_3	4.88	4.98	5.37	4.71	4.54	2.37	5.30	4.54	5.07
TiO_2	0.11	0.09	0.07	0.12	0.10	0.09	0.13	0.08	0.08
P_2O_5	31.77	26.71	25.00	33.58	26.54	25.19	34.36	30.97	24.86
MnO	0.37	0.33	0.28	0.40	0.31	0.30	0.40	0.30	0.28
ZnO	0.15	0.40	0.35	0.08	0.38	0.35	0.15	0.37	0.35
Others[*]	0.82	4.15	5.41	1.24	5.24	5.32	0.34	5.12	5.55
LOI	1.58	9.41	13.04	1.73	10.38	16.99	0.21	8.35	12.68
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[*] Microelements and chlorine

product obtained from the combustion of poultry litter in fluidized bed combustion technology (Lynch et al. 2013). For comparison, ash from phosphate rocks from Khouribga rock phosphate (Morocco) contained 33 wt.% of P_2O_5 (Kley et al. 2003) while the chemical composition of the phosphate rocks provided by the General Company of Phosphate and Mineral Resources contain 15.42 wt.% P_2O_5 for low-grade and 37.19 wt.% P_2O_5 for high-grade Syrian phosphate (Safi et al. 2006). The research shows, however, that the phosphorus content in chicken poultry ashes may also be lower. This is evidenced by the work carried out by Huang et al. (2011), who combusted chicken manure from the caging of layers, obtaining P_2O_5 yield in the range of 4.5-7.5 wt.% at 400-900 °C, respectively.

In the studies conducted by Staroń et al. (2016) in the temperature range of 600-900 °C, the total phosphorus content calculated as P_2O_5 amounted to: 14.7-17.4 wt.%,

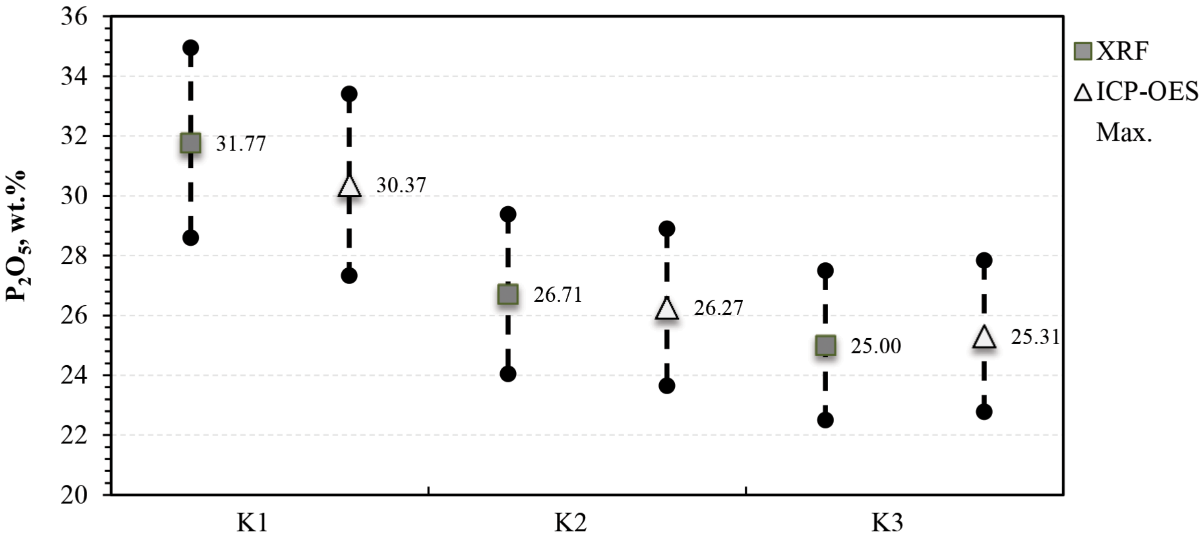

Fig. 2 Comparison of P_2O_5 content (wt.%) in ash obtained from XRF and ICP-OES analysis taking into account the measurement uncertainty±10%

with a burning time of 1h and 15.8-17.9 wt.%, at 3h. On the basis of thermogravimetric analysis (TG), the same authors proved that the process of combustion of manure samples took place in three stages. The exothermic effect was observed relating to the ignition temperature approx. 280 °C and the weight loss in temperature range of 300-500 °C. The organic fraction combustion process was terminated below 600 °C. A similar content of P_2O_5 in ashes from chicken manure was obtained after 3 hours of combustion at 600 °C and 900 °C and amounted to 8.8-12.8 wt.% and 12.5-14.8 wt.%, respectively (Wzorek et al. 2008). The obtained test results of samples K1-K9 proved the great potential of using these ashes for the production of agricultural fertilizers as substitutes for phosphate rocks.

In addition, the analysis of the microelements contained in the ashes obtained (Table 4) showed the absence of arsenic, which is very toxic to the environment and can negatively affect the state of the soil ecosystem (Jayasumana et al. 2015). Samples contained trace amounts of chromium, cobalt, cadmium and molybdenum (0-8ppm) and small amounts of lead (<20ppm) and nickel (<45ppm). The concentrations of these elements were within the limits for agricultural fertilizers stipulated in Polish regulations (Minister of Agriculture and Rural Development 2008). The highest amount of microelements was determined for bromine (886-5839 ppm) and strontium (502-613ppm). In addition, the analysis showed that the increase in combustion temperature from 500 °C to 900 °C reduced the copper and bromine content threefold. An opposite trend was observed in the case of strontium content. Higher temperature contributed to a slight increase in the content of this element in the sample.

XRD analysis

Diffractometric studies allowed the recognition of the mineral composition of chicken manure ash as well as the calculation of the amount of crystalline mineral phases and amorphous substance. Samples with symbols K1, K2 and K3 were selected for the tests, and then combusted for 5h at 900, 700 and 500 °C, respectively. Ash analysis (Table 5) showed that the main mineral crystalline phase was whitlockite (β-$(Ca,Mg)_3(PO_4)_2$); sylvite (KCl) and calcite ($CaCO_3$). Whitlockite present in the samples was found to be closest to the PDF 04-010-2972 standard with the general formula $Ca_{2.7}Mg_{0.3}(PO_4)_2$. This mineral is most often found in phosphorite deposits and guano. Its content was similar in each tested ash sample, amounting to 21.32-23.35 wt.%. As the reference literature data shows (Bergfeldt et al. 2018) the main component of the raw manure accounting for over 50% of its contents is usually calcium carbonate (calcite). Dolomite, anhydrite, plagioclase, hematite and quartz are present in smaller amounts. At temperatures above 500 °C, calcium carbonate decomposes to calcium oxide, as seen in samples K2 and K1, where the amount of CaO increased to 4.10 and 11.17 wt.%, respectively. The obtained results were consistent with the research conducted in Poland so far (Wzorek et al. 2008). At 700 °C, the formation of water-insoluble aluminium phosphate ($AlPO_4$) and calcium phosphate $Ca_3(PO_4)_2$ was also observed. The content of these substances in samples K1

Table 4 Microelements contents of ash (ppm) depend on time and temperature of combustion

Parameter	Ash sample								
	K1	K2	K3	K4	K5	K6	K7	K8	K9
T(°C)/time (h)	900/5	700/5	500/5	900/3	700/3	500/3	900/8	700/8	500/8
As	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ba	80	58	6	66	bdl	9	66	24	30
Br	bdl	bdl	bdl	886	2543	5839	1480	3096	3311
Cd	3	bdl	11	bdl	bdl	bdl	8	8	2
Co	bdl	bdl	bdl	6	4	bdl	2	1	bdl
Cr	bdl	bdl	bdl	bdl	bdl	1	3	bdl	bdl
Cu	146	337	352	110	396	256	131	320	344
Ga	bdl	bdl	bdl	8	8	5	2	9	9
I	bdl	bdl	bdl	45	6	86	42	12	bdl
Mo	bdl	bdl	bdl	8	bdl	1	5	bdl	bdl
Ni	38	28	25	41	31	31	42	30	36
Pb	14	18	15	bdl	2	19	16	1	15
Rb	51	82	80	48	70	73	55	74	68
Se	bdl	bdl	bdl	bdl	bdl	14	bdl	bdl	3
Sr	595	551	502	608	548	508	613	548	510
V	29	23	27	16	13	25	17	28	10
Zr	bdl	bdl	bdl	139	126	118	141	125	116
Total	956	1097	1018	1981	3747	6985	2623	4276	4454

bdl-below detection limit

and K2 was 6.09 and 6.15 wt.% for $AlPO_4$ and 12.18 and 7.18 wt.% for $Ca_3(PO_4)_2$. A small amount, i.e. 2.03% of the substance of the formula $Ca_2SiO_4.Ca_3(PO_4)$ could be observed at the temperature of 900 °C. In the investigated samples the following crystalline solids contained phosphorus were identified:

- whitlockite β-$(Ca,Mg)_3(PO_4)_2$,
- iron(II) phosphate $Fe_3(PO_4)_2$,
- arcanite $AlPO_4$,
- sodium phosphate Na_3PO_4,
- calcium phosphate $Ca_3(PO_4)_2$,
- calcium silicate/calcium phosphate $Ca_2SiO_4.Ca_3(PO_4)_2$.

Besides crystalline minerals the samples tested also contained from 14.72 to 24.87 wt.% of amorphous substance, which decreased with the increasing combustion temperature of the sample. It is believed that the main component of phosphorus in the amorphous phase is non-crystalline calcium orthophosphates ($CaPO_4$) (Dorozhkin 2017) or another amorphous form of this element. The ratio of the crystalline phase/amorphous phase calculated on the basis of weight proportions was: 6/1(K1), 4/1 (K2), and 3/1 (K1), respectively.

The determined crystalline phases in the samples are shown in the Figs (3-5). Due to the large amounts of mineral phases, only the strongest reflections of the crystalline phases were determined. Explanations of the letter symbols of the crystalline phases on the diffractometers are provided in Table 5.

On the basis of the ICP-OES and XRD test results in K1-K3 ash samples and the phosphorus molar share in crystalline components containing phosphorus (W, F, P, X, C, Z), the estimated content of P_2O_5 crystalline phase (Pc ,wt.%) calculated according to the equation (1) and is presented in Table 6.

Table 5 Phase composition (wt.%) of ashes from chicken manure using the XRD method. Average values (SD) ±1.0 wt.%

n	Name and chemical formula of crystalline phase		Sample		
			K1	K2	K3
W	Whitlockite	β-$(Ca,Mg)_3(PO_4)_2$	23.35	21.54	21.32
Y	Sylvite	KCl	0.00	11.28	11.17
K	Calcite[*]	$CaCO_3$	5.58	5.64	10.66
A	Anhydrite	$CaSO_4$	2.03	2.05	9.14
F	Iron(II) phosphate	$Fe_3(PO_4)_2$	4.06	5.13	5.08
N	Nyerereite	$Na_2Ca(CO_3)_2$	0.00	0.00	4.06
R	Arcanite	K_2SO_4	9.14	6.15	3.05
P	Aluminium phosphate	$AlPO_4$	6.09	6.15	0.00
V	Calcium oxide	CaO	11.17	4.10	0.00
Q	Quartz[*]	SiO_2	2.54	3.59	2.54
X	Sodium phosphate	Na_3PO_4	0.00	0.00	1.02
H	Halite	$NaCl$	0.00	1.03	1.02
C	Calcium phosphate	$Ca_3(PO_4)_2$	12.18	7.18	0.00
Z	Calcium silicate/Calcium phosphate	$Ca_2SiO_4 \cdot Ca_3(PO_4)_2$	2.03	0.00	0.00
S	Potassium feldspar, Albite, Anorthite	$K[AlSi_3O_8]$, $Na[AlSi_3O_8]$, $Ca[Al_2Si_2O_8]$	7.11	7.18	6.09
Total amorphous phase[*]			14.72	18.97	24.87
Total crystalline phase			85.28	81.03	75.13

n-symbol of crystalline phase component

[*] Average values (SD) ± 0.5 wt.%

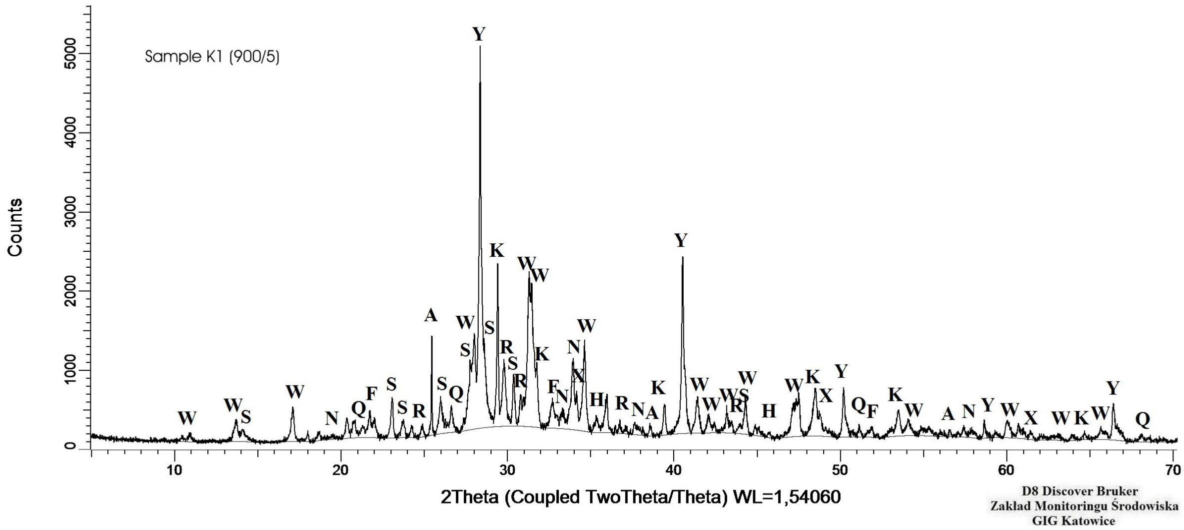

Fig. 3 X-ray diffractogram of the ashes from chicken manure of sample K1
The phase symbols was explained in Table 5

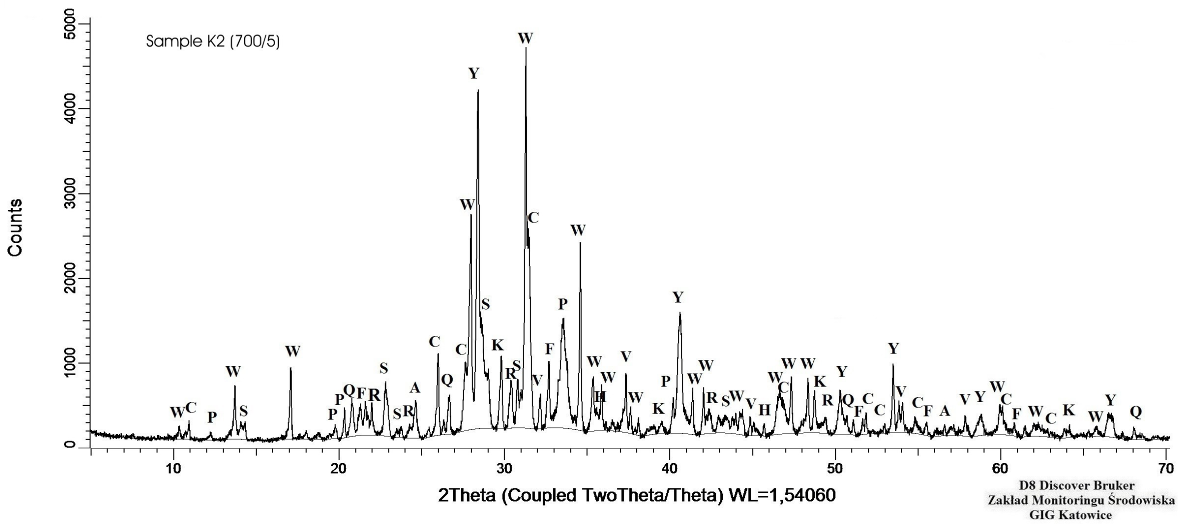

Fig. 4 X-ray diffractogram of the ashes from chicken manure of sample K2
The phase symbols was explained in Table 5

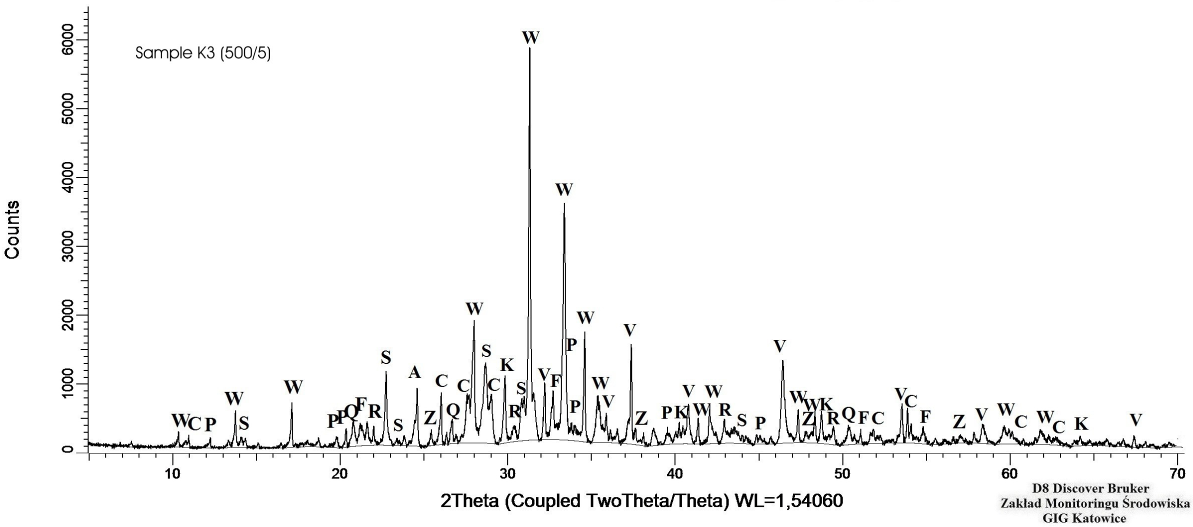

Fig. 5 X-ray diffractogram of the ashes from chicken manure of sample K3
The phase symbols was explained in Table 5

$$Pc = \sum \frac{CP_n \cdot S_n}{M_n} \qquad (1)$$

where:
CP_n –is "n" crystalline phase content in the sample according to XRD analysis, wt.%
S_n – is molar share of P_2O_5 in "n" crystalline phase component
M_n – is molar mass of "n" crystalline phase component
n – is crystalline phase component containing phosphorus: W, F, P, X, C, Z (according the Table 5)

Estimated P_2O_5 content for the amorphous phase (Pa, wt.%) was calculated according to the equation (2):

$$Pa = Pt - Pc \qquad (2)$$

where:
Pt– is total P_2O_5 content in the sample (K1, K2 or K3) according to the ICP-OES analysis, wt.%
Pc – is P_2O_5 content in the crystalline phase, wt.% according to the equation (1)

Table 6 Total P_2O_5 content in crystalline phase (Pc) and P_2O_5 content in n crystalline phase component (Pc_n) of ash samples K1-K3

n	Chemical formula of Pc	Pc_n K1	K2	K3
W	$Ca_{2.7}Mg_{0.3}(PO_4)_2$	10.86	10.02	9.92
F	$Fe_3(PO_4)_2$	3.22	4.07	4.03
P	$AlPO_4$	3.54	3.58	0.00
X	Na_3PO_4	0.00	0.00	0.88
C	$Ca_3(PO_4)_2$	5.58	3.29	0.00
Z	$Ca_2SiO_4{\cdot}Ca_3(PO_4)_2$	0.60	0.00	0.00
	Pc	**23.80**	**20.96**	**14.83**

Based on the result of total P_2O_5 contained in the crystalline and amorphous phases detected by ICP-OES analysis (Fig. 2), the content of crystalline phase of P_2O_5 estimated according to the equation (1) increased with increasing sample combustion temperature and was respectively: 14.83 wt.% at 500 °C (K3), 20.96 wt.% at 700 °C (K2) and 23.80 wt.% at 900 °C (K1). The calculated P_2O_5 content in the crystalline phase (Pc) is provided in Fig. 6.

The content of the amorphous phase of P_2O_5 estimated according to the equation (2) is provided in Fig. 7.

The calculated P_2O_5 content in the amorphous phase (Pa) decreased with increasing sample combustion temperature and was respectively: 14.83 wt.% (500 °C), 20.96 wt.% (700 °C) and 23.80 wt.% (900 °C). Based on the calculations made, it was found that the highest P_2O_5 content in the amorphous phase was per sample burned at 500 °C. The calculated content of

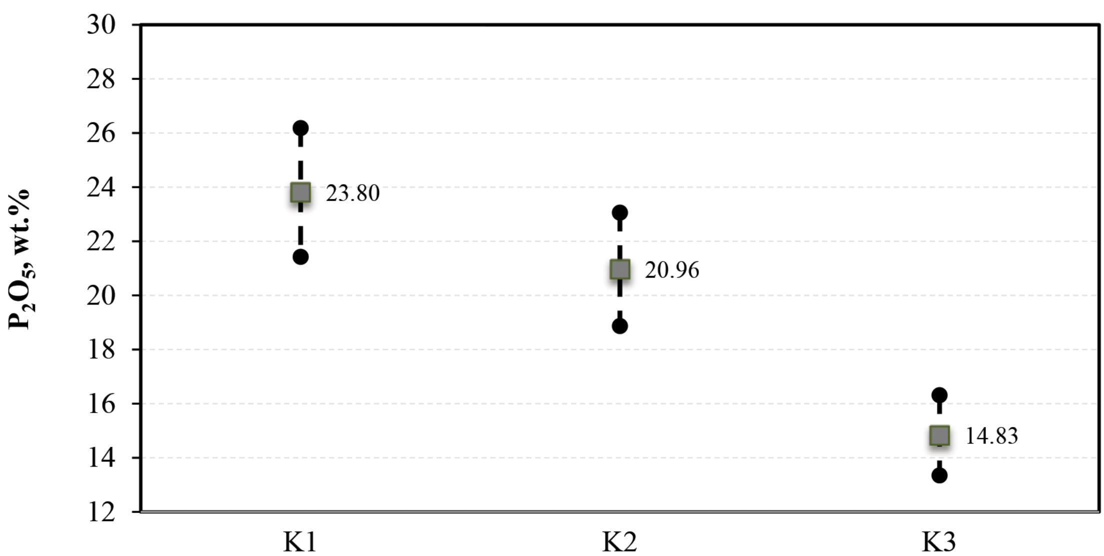

Fig. 6 Estimated P_2O_5 content in crystalline phase (Pc) of ash samples (K1, K2, K3) taking into account the measurement uncertainty ±10%

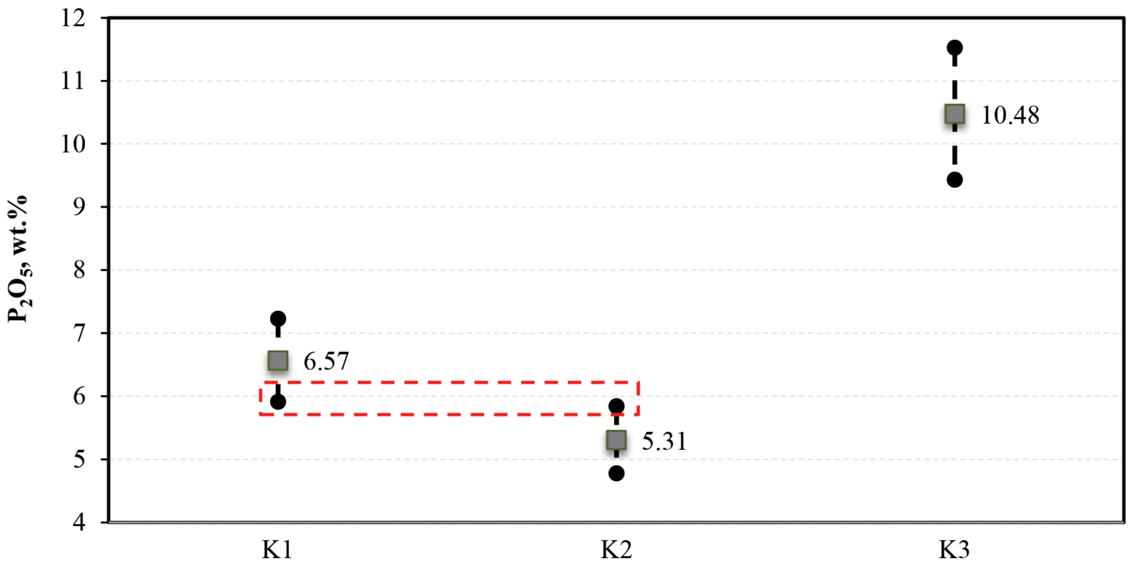

Fig. 7 Estimated P_2O_5 content in amorphous phase of ash samples (K1, K2, K3) taking into account the measurement uncertainty±10%

amorphous P_2O_5 in sample K3 amounted to 10.48 wt.% and was significantly higher than in samples K1 and K2, burned 5.31 wt.% at 700 °C and 6.57 wt.% at 900 °C. These results confirm the analysis of the total phosphorus content in the ash extracts presented in Table 7. It is expected that the results obtained will be used at a later stage of the research in order to optimize the phosphorus recovery methodology through extraction from chemical solutions.

Photometer analysis

Egner-Riehm method, which is a method commonly applied in Poland to assess the content of available phosphorus in soils, was used in the study (Tyszkiewicz et al. 2019). It is assumed that the phosphorus forms extracted with calcium lactate solution ($C_6H_{10}CaO_6$) closely correspond to the amount of phosphorus available for plants. The solution used for extraction is well buffered, both for hydrogen ions and calcium ions, which significantly affect the solubility of phosphorus compounds in soil. The obtained extracts were colourless, which enabled their colorimetric determinations. The results of tests performed on the content of P, mg/l in samples K1-K3 are shown in Table 7.

The analysis showed that the phosphorus content in ash extracts indicated a linear relationship between the combustion temperature of the manure sample and the amount of leachable phosphorus content. The highest P concentration 0.9 mg/l was determined for the K3 sample combusted at 500 °C, and the lowest for the K1 sample (900 °C). The amount of phosphorus in the water extract for sample K1 was <0.01 mg/l, i.e. below detection limit. The content of available P in Egner-Riehm solution indicated that the amount of this element in sample K3 (500 °C) was 146.8 mg/l and was significantly higher than the amount of P determined in samples K2 (700 °C) and K3 (900 °C) - 10.9 and 4.0 mg/l, respectively.

Conclusion

The use of biowaste in the form of poultry manure as a raw material for the production of mineral fertilizers offers an alternative to replacing phosphate rocks that are already depleted. The best solution to transform poultry manure into a phosphorus source is its prior combustion, followed by extraction in chemical solutions, allowing to determine the amount of phosphorus contained in the ashes in a form available to plants.

Table 7 Determination of total phosphorus content in ash extracts by photometric method

Ash sample	Total P (H_2O) mg/l P	Scope of the method mg/l P	Total P (CaL) [b] mg/l	Scope of the method mg/l
K1	bdl[a]	0.01-1.5	4.0	0.2-5.0
K2	0.03	0.01-1.5	10.9	5.0-50.0
K3	0.9	0.2-5.0	146.8[c]	5.0-50.0

[a] bdl-below detection limit

[b]CaL-calcium lactate ($C_6H_{10}CaO_6$)

[c]determined by diluting sample with water in ratio 1:3

Moreover, the combustion of poultry manure offers additional benefits, such as reduction in waste mass with simultaneous decrease in the biological threat and odour nuisance.

The chemical compositions of ashes from poultry manure differ significantly and depend on the combustion technique used. The analysis of the chicken manure combustion process showed that the key parameter affecting the quality of the ash obtained is the temperature used. The content of the P_2O_5 detected by ICP-OES and XRF analysis showed comparable values, 30.37 wt.% and 31.77 wt.% at 900 °C, 26.27 wt.% and 26.71 wt.% at 700 °C and 25.31 wt.% and 25.00 wt.% at 500 °C, respectively.

The mineral composition of chicken manure ashes detected by XRD analysis divided them into two fractions: crystalline and amorphous, the estimated values of P_2O_5 content in crystalline phase being 14.83 wt.% at 500 °C, 20.96 wt.% at 700 °C, and 23.80 wt.% at 900 °C and grew along with the increase of combustion temperature. The estimated P_2O_5 contents in the amorphous phase of ash samples were 10.48 wt.% at 500 °C, 5.31 wt.% at 700 °C, and 6.57 wt.% at 900 °C, which leads to the conclusion that increasing the temperature over 700 °C has no significant effect on the amount of phosphorus generated in the process.

The diffractometric tests of the ashes obtained and the photometric analysis of the extracts obtained from them confirm that the amorphous phase may offer/present a valuable source of bioavailable phosphorus. Despite that, the best leaching effects of phosphorus compounds, using the Enger-Rhiem solution, were obtained for manure burned at 500 °C. The amount of phosphorus determined for this sample was 146.8 mg/l and was significantly higher than the amount of this element in samples burned at 700 °C (10.9 mg/l) and 900 °C (4.0 mg/l). Thermal treatment of poultry manure towards phosphorus recovery may partially solve the problem of managing that troublesome biowaste. Studies show that the currently economically unprofitable process of phosphorus recovery from incinerated manure appears to be more efficient. A higher quality product in terms of available phosphorus content may be obtained by using lower combustion temperature. It is possible to obtain a higher quality product in terms of available phosphorus content by using a combustion temperature below 700 °C.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

References

Baki Unal H, Bayraktar H, Illkay Alkan R, Cengiz Akdeniz R (2015) Evaluation possibilities of chicken manure in Turkey. Agric Eng 2 (254): 5–14. https://doi.org/10.14654/ir.2015.154.116

Bergfeldt B, Morgano MT, Leibold H,Richter F, Stapf D (2018) Recovery of phosphorus and other nutrients during pyrolysis of chicken manure. Agric 8 (187): 1–10. https://doi.org/10.3390/agriculture8120187

Bicudo JR, Goyal SM (2003) Pathogens and manure management systems: A review. Environ Technol 24 (1): 115–130. https://doi.org/10.1080/09593330309385542

Bolan NS, Szogi AA, Chuasavathi T, Seshadri B, Rothrock JR, Panneerselvam P (2010) Uses and management of poultry litter. Worlds Poult Sci J 66 (4): 673–698. https://doi.org/10.1017/S0043933910000656

Chen Z, Jiang X (2014) Microbiological safety of chicken litter or chicken litter-based organic fertilizers: A review. Agriculture 4: 1–29. https://doi.org/10.3390/agriculture4010001

Ciesielczuk T, Rosik Dulewska C, Kusza G (2016) Extraction of phosphorus from sewage sludge ash and sewage sludge-problem analysis. Polish J Sustain Dev 20: 21–28. https://doi.org/10.15584/pjsd.2016.20.3

Correll DL (1998) Role of phosphorus in the eutrophication of receiving waters: A review. J Environ Qual 27: 261–266. https://doi.org/10.2134/jeq1998.00472425002700020004x

Dorozhkin SV (2017) Hydroxyapatite and other calcium orthophosphates: Nanodimensional, multiphasic and amorphous formulations. Nova Science Publishers, Moscow, Russia

Elliott JC (1994) Structure and chemistry of the apatites and other calcium orthophosphates, 1st Edition Elsevier Science, Amsterdam, The Netherlands 18: 1-404

Gilbert N (2009) Environment: The disappearing nutrient. Nature 461: 716–718. https://doi.org/10.1038/461716a

Havukainen J, Nguyen MT, Hermann L, Horttanainen M, Mikkilä M, Deviatkin I, Linnanen L (2016) Potential of phosphorus recovery from sewage sludge and manure ash by thermochemical treatment. Waste Manag 49: 221–229. https://doi.org/10.1016/j.wasman.2016.01.020

Huang Y, Dong H, Shang B, Xin H, Zhu Z (2011) Characterization of animal manure and cornstalk ashes as affected by incineration temperature. Appl Energy 88: 947–952. https://doi.org/10.1016/j.apenergy.2010.08.011

Jasinski SM (2019) Phosphate rock. U.S. Geological Survey, Mineral Commodity Summaries, 122-123

Jayasumana C, Fonseka S, Fernando A, Jayalath K, Amarasinghe M, Siribaddana S, Gunatilake S, Paranagama P (2015) Phosphate fertilizer is a main source of arsenic in areas affected with chronic kidney disease of unknown etiology in Sri Lanka. Springerplus 4:1–8. https://doi.org/10.1186/s40064-015-0868-z

Kelleher BP, Leahy JJ, Henihan A, O'Dwyer TF, Sutton D, Leahy MJ (2002) Advances in poultry litter disposal technology - A review. Bioresour Technol 83: 27–36. https://doi.org/10.1016/S0960-8524(01)00133-X

Kley G, Köcher P, Brenneis R (2003) Möglichkeiten zur Gewinnung von Phosphor-Düngemitteln aus Klärschlamm-, Tiermehl- und ähnlichen Aschen durch thermochemische Behandlung, Tagungsband zum Symposium "Rückgewinnung von Phosphor in der Landwirtschaft und aus Abwasser und Abfall", UBA Berlin und RWTH Aachen, Berlin, Germany

Kucharski P, Białecka B (2019) Poultry manure as a substrate for agriculture and the chemical industry. In: 19th International multidisciplinary scientific GeoConference. Section Ecology and Environmental Protection. Bulgaria

Li B, Boiarkina I, Yu W, Ming Huang H, Munir T, Qian Wang G, Young BR (2019) Phosphorus recovery through struvite crystallization: Challenges for future design. Sci Total Environ 648: 1244–1256. https://doi.org/10.1016/j.scitotenv.2018.07.166

Łuczkowska D, Kuźdżał E, Cichy B (2016) Study on the reactivity of phosphorites. Przem Chem 95(8): 1538–1541. https://doi.org/10.15199/62.2016.8.24

Lynch D, Henihan AM, Bowen B, Lynch D, McDonnell K, Kwapinski, Leahy JJ (2013) Utilisation of poultry litter as an energy feedstock. Biomass and Bioenergy 49: 197–204. https://doi.org/10.1016/j.biombioe.2012.12.009

Minister of Agriculture and Rural Development (2008) Regulation of 18 June 2008 on the implementation of certain provisions of fertilizers and fertilization. Journal of Law 119 (765) 6515-6520 (in Polish)

Myszograj S, Puchalska E (2012) Waste from rearing and slaughter of poultry – treat to the environment or feedstock for energy. Environ Med 15 (3): 106–115 (in Polish)

Othake H, Tsuneda S (2019) Phosphorus recovery and recycling. Springer Nature, Singapore. https://doi.org/10.1007/978-981-10-8031-9

Pavlostathis S, Giraldo-Gomez E (1991) Kinetics of anaerobic treatment: A critical review. Crit Rev Environ Control 21 (5-6): 411–490. https://doi.org/doi.org/10.1080/1064338910938842

Reinhard CT, Planavsky NJ, Gill BC, Ozaki K, Robbins KJ, Lyons TW, Fisher WW, Wang C, Cole DB, Konhauser KO (2017) Evolution of the global phosphorus cycle. Nature 541: 386–389. https://doi.org/10.1038/nature20772

Safi MJ, Bhagwanth Rao M, Surya Prakash Rao KS, Govil PK (2006) Chemical analysis of phosphate rock using different methods - Advantages and disadvantages. X-Ray Spectrom 35: 154–158. https://doi.org/10.1002/xrs.886

Samreen S, Kausar S (2016) Phosphorus Fertilizer: The original and commercial sources. In: IntechOpen. 6: 81-94. http://dx.doi.org/10.5772/intechopen.82240

Sengul H, Ozer AK, Gulaboglu MS (2006) Beneficiation of Mardin-Mazidaği (Turkey) calcareous phosphate rock using dilute acetic acid solutions. Chem Eng J 122: 135–140. https://doi.org/10.1016/j.cej.2006.06.005

Staroń P, Kowalski Z, Staroń A, Seidlerová J, Banach M (2016) Residues from the thermal conversion of waste from the meat industry as a source of valuable macro- and micronutrients. Waste Manag 49:337–345. https://doi.org/10.1016/j.wasman.2016.01.018

Statistics Poland (2017) Statistic yearbook of the Republic of Poland. Central Statistical Office, Warsaw, Poland (in Polish)

Steen I (1998) Phosphorus availability in the 21st century: Management of a non-renewable resource. Phosphorus and Potassium 217: 25–31

Tyszkiewicz Z, Czubaszek R, Roj-Rojewski S (2019) Basic methods of laboratory soil analysis. Bialystok University of Technology. https://doi:10.24427/978-83-65596-89-5 (in Polish)

Van Straaten P (2002) Rock for crops. International Centre for Research in Agroforestry, Nairoby, Kenya, 1-348

Van Voorneburg F, Van Ruiten LHAM, Have PJW (1998) Phosphate recovery from animal manure the possibilities in the Netherlands. Report CEEP. Brussels, Belgium

Van Vuuren DP, Bouwman AF, Beusen AHW (2010) Phosphorus demand for the 1970-2100 period: A scenario analysis of resource depletion. Glob Environ Chang 20: 428–439. https://doi.org/10.1016/j.gloenvcha.2010.04.004

Vance CL (2019) LSU Digital commons using poultry litter ash as a fertilizer source for Bermudagrass (*Cynodon dactylon*) Establishment and loblolly pine (*Pinus taeda*) plantation. LSU Doctoral Dossertations. 5099. Louisiana State University and Agricultural and Mechanical College. https://digitalcommons.lsu.edu/gradschool_dissertations/5099

Wu D, Li L, Zhao X, Peng Y, Yang P, Peng X (2019) Anaerobic digestion: A review on process monitoring. Renew Sustain Energy Rev 103: 1–12. https://doi.org/10.1016/j.rser.2018.12.039

Wzorek Z, Krupa-Żuczek K, Bajcer T (2008) Possibility of phosphorus recovery from dung from chicken-farms. Arch Waste Manag Environ Prot 7: 21–28 (in Polish)

Yokota T, Ito T, Saigusa M (2003) Measurement of total phosphorus and organic phosphorus contents of animal manure composts by the dry combustion method. Soil Sci Plant Nutr 49 (2): 267–272. https://doi.org/10.1080/00380768.2003.10410006