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Possibility to eliminate emission of odor from pig manure treated using AMAK filtration method

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ABSTRACT

Odor concentration in samples of gases taken from above the surface of raw pig manure and also the manure treated using a filtration method was measured. It was found out that pig manure mineralization and the filtration technology (the AMAK process) enables almost complete elimination of odor emission from post-filtration sludge and filtrate. The grade of treated manure neutralization made with the use of lime milk was found to be the most significant parameter affecting intensity of odor emission when applying a filtration method. An increase in pH value from 8.0 to 10.5 caused reduction of odor concentration by 99.1 and 99.5% in the samples taken from above the filtrate and the post-filtration sludge, respectively, comparing to the odor concentration found in the samples taken from above raw pig manure. For the tested samples, which were taken from above the fertilizer produced on the basis of post-filtration sludge coming from treated pig manure, the lowest odor concentration was 97% less than the value obtained for raw pig manure. The odor concentration in the samples taken from above the filtrate and the sediment obtained in the proposed filtration method was lower than the average value of odor concentration above pig manure lagoon by 90.5 and 94.5%, respectively.

Keywords: Pig manure; Filtration; Odor emission

1. Introduction

Stock breeding is strictly connected with production and emission of malodorous substances into ambient air. One of the largest sources of such emission is pig manure. It comprises approx. 400 foul-smelling volatile organic and inorganic compounds, including ammonia and hydrogen sulfide. These substances have a different chemical structure and odor intensity. Malodorous substances present in pig manure are grouped in 12 groups of organic compounds and one group of an inorganic one, and ammonia is the main component [1,2].

The studies [1–4] have proven that intensity of malodorous substance emission depends to a consid-

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erable extent on piggery arrangement. Pig physiology also has a deciding impact on emission of malodorous substances. The studies [2,4,5] analyzed odors emitted by pig manure produced by reproductive sows, fatteners, and piglets taken from nursing. Thirty-five substances belonging to different groups of chemical compounds were found. It was found out [2] that the largest ammonia and hydrogen sulfide emission occurred during fattener breeding.

The methods used to control emission of malodorous substances may be either direct or indirect. Direct methods are based on the modification of feed additives (e.g. humic acid-based preparations) to reduce nitrogen excretion, and/or on modification of protein composition and reduction of the content of proteins and sulfur-bearing substances in the fodder [1]. In [6] bismuth compounds, complexes of copper and chlorophyll and powdered activated charcoal are used as the additives to fodder to provide so called internal disinfection enabling reduction of odor emission [5]. It was demonstrated that the content of raw proteins in fodder affects the emission of nitrogen compounds (mainly ammonia-based ones). Reduction of the raw protein content in the fodder to 12.5% enabled reducing the content of ammonia-based nitrogen by 43% comparing to the fodder bearing 16.5% raw proteins [5].

In the case of biological and combined biological and enzymatic methods, controlling odor emission is possible owing to the use of selected strains of anaerobic bacteria, for example *Geobacter, Geovibro,* and *Geothrix* soil bacteria [1]. Using biofilters in piggeries brings also good effects regarding the control of odor emission. In the study [7], biofiltration of outlet air from piggery with the use of two types of filtration beds is described. The basis of both filtration beds was vegetable soil (40%) and peat (40%), while the additives were either straw (20%) or oak chips (10%) with crushed oak bark (10%). Efficiency of air cleaning amounted to 65% [7]. Thermal processes [8] with the use of oxidizers are increasingly important in food industry. The BIOSORTM-Manure biofiltration process [9] implemented to pig farming in Canada reduced the concentration of odors emitted during production and storage of pig manure by ≥80%.

To reduce the emission of odorous from pig manure air, aeration or ozonation treatment, both in gaseous and liquid phases, is carried out [1,10]. Ozone treatment of the manure causes noticeable reduction of indole and phenol compound concentration. Furthermore, emission of all sulfides comprised in pig manure is efficiently prevented and, as a result, the general emission of odor from pig manure is noticeably reduced [11]. Pig manure aeration supports intensification of processes running in aerobic conditions. According to [12], aeration reduced emission of odor from pig manure. The lowest losses of ammonia were observed during storage of pig manure treated in anaerobic conditions ($10\ g\ m^{-3}$) [13]. Anaerobic digestion of pig manure offers numerous benefits such as methane production and reduction of environment pollution and odor emission [14].

Most malodorous organic compounds come from solid waste; therefore, separation of pig manure into solid and liquid fractions may reduce emission of odor from the manure. Reduction of noxious odor depends to considerable extent on the content of organic solids and nutritional ingredients, which undergo biodegradation. Nevertheless, according to [11], separated liquid fraction is still dark brown and foul-smelling. Intensity of odor depends on the content of organic substances remaining in the liquid. Therefore, additional treatment of liquid fraction is usually required. According to [12], contents of volatile fatty acids (VFA), phenols, and indoles may be deemed odor indicators. Therefore, when analyzing effects of separation (on screens) on odor emission, VFA content was determined using the extraction method. Maximum reduction of odor emission was observed in the case of samples with the particle diameter <0.075 mm. On the other hand, no significant differences in VFA emission were found in the case of samples whose particle diameters were within the range of 0.15–2.0 mm [11].

The use of membrane methods, which require pretreatment of pig manure using separation techniques, enables meeting the requirements of environmental protection in terms of pig manure management [15]. Pig manure produced during intensive pig farming at industrial scale has to be properly managed in order to reduce odor emission and transportation and storage costs. Prior to further treatment, pig manure has to be separated into solid and liquid phases using membrane methods [16–18].

Our previous studies allowed for developing an effective method of pig manure treatment by filtration resulting in reduction of odor emission from above filtrate and sediment by –75% [19–22]. Filtrate may be used to sprinkle irrigation of crops and sediment to produce combined mineral and organic fertilizers [21,23]. In this study, the results of studies on effects of selected parameters of pig manure treatment, using AMAK method, on odor concentration in samples taken from above raw pig manure, products of its filtration (filtrate and post-filtration sludge) and combined mineral and organic fertilizer produced from the sludge are discussed. The developed AMAK process of pig manure mineralization and filtration [19,20,23] is composed of several stages. Pig manure being continuously stirred is treated at first with phosphoric acid and, subsequently, with sulfuric acid to reach pH –5.5 and –3.0, respectively, then, 10% solution of lime milk is added to neutralize the slurry to obtain pH > 8. The treatment with the use of mineral acids is aimed at transforming macro-and micro-fertilizer components into the form bio-accessible to the plants and at binding of volatile organic and inorganic nitrogen-bearing compounds (for reduction of nitrogen losses during storage and use) and hydrolysis and mineralization of organic matter [19,24]. Afterward, superphosphate is added in the amount of approx. 4% of the initial pig manure weight. Next, 10% solution of lime milk is applied to neutralize the slurry to appropriate pH value pH > 8. Subsequently, entire slurry is boiled and filtered on a periodic pressure filter (or filter press).

2. Materials and methods

The pig manure treated and separated in treatment and the filtration AMAK process into sediment and filtrate was taken to tests. The possibility of controlling the mineralization process of pig manure slurry to obtain filtrate and sludge of the best quality was studied. It was found out that the application of an appropriate amount of lime milk in two-stage mineralization process contributes to improvement of obtained product quality by almost entirely eliminating odor emission and by reducing the minimum of the phosphorus content in a liquid phase [20,23]. Owing to this treatment, phosphorus, which is the main component of fertilizers, passes almost entirely to a solid phase used to produce mineral–organic fertilizers [21].

2.1. Treatment of pig manure slurry

Odor concentration was determined for the samples of gases taken from above raw pig manure before mineralization, filtration products of treated pig manure (sediment and filtrate) and produced fertilizers. Sediment and filtrate of pig manure were obtained using the AMAK method [19,23], while the samples of selected fertilizers were prepared using the methodology [21,23]. The sediment from filter press is mixed with mineral additives in a single-shaft mixer to obtain combined a mineral and organic fertilizer [21] of universal nature. The filtrate is directed to a storage tank, from where it can be delivered to waste water treatment plant or taken in order to sprinkle irrigation of crops [19,23].

2.2. Experimental procedure

The objective of the study was to determine the effects of selected pig manure treatment parameters, particularly parameters of neutralization, on the rate of odor emission. The odor concentrations and the values of specific odor emissions from the samples of gases taken from above pig manure before mineralization, post-filtration sludge, filtrate and a fertilizer were determined. Moreover, the odor emissions produced by samples taken from pig manure lagoon were compared and assessed [22].

Preliminary tests showed that the final pH of treated manure influenced on odor emission from sediment and filtrate. In our tests (in details presented in Table 1), pig manure was treated at first with phosphoric acid, and subsequently, with sulfuric acid. Then, to reach predicated pH, a solution of lime milk, and subsequently, superphosphate was added. In the second stage of neutralization, also lime milk solution was added to reach predicated pH, and subsequently, the whole mixture was heated and filtered.

2.3. Measurements of odor emission

Odor concentrations were measured using a dynamic olfactometric method, and the procedures described in [23,25–27]. The measurements of odor concentration were made for gases taken from above a pig manure lagoon and for gases taken from above laboratory samples of pig manure before mineralization, filtrate, sediment, and a fertilizer. Sketches and operating conditions of the test stand developed for the studies are described in [22,23]. The samples were taken in an averaged time of 30 s, 5 min, and 30 min using appropriate samplers [22,23,25,27].

A four-stand olfactometer of TO8 type with necessary fittings was used to measure odor concentrations. According to the standard [25,27], the measurements were made in a soundproof isolated room of stable temperature and lighting conditions. The measurement team was composed of four people for testing and one operator. People were selected for testing in accordance with the guidelines comprised in the standard using a reference substance n-butanol in nitrogen. The tests in an olfactometer chamber were carried out without any forced and turbulent flow caused by a fan (it was not used), on the assumption of stagnation conditions (zero velocity of wind). Under such conditions (no ventilation above surface of the sample tested), odor emission should be maximum.

Blank samples composed of pure, odorless air were also taken to test. The olfactometer was connected with a PC with special software installed. Each

Table 1
Characteristic of pig manure mineralization and filtration process parameters and samples for odor concentration measurements

No.	Quantity of raw materials used (g)/final pH					Filtration parameters			Sediment		Filtrate	
	Pig manure	H_3PO_4 (pure, 75%)	H_2SO_4 (tech. 95%)	Lime milk (10% solution)	Super-phosphate	Time (s)	Temp. (˚C)	Pressure (bar)	Weight (g)	Moisture content (%)	Weight (g)	pH
1	230.2/7.4	3.7/5.5	2.7/3.0	32.0[1]/8.0 5.5[2]/8.0 37.5[3]	9.2/5.5	30	70.0	2.5	58.0	60.5	173.0	4.4
2	230.1/7.4	3.3/5.5	2.6/3.0	25.3[1]/8.5 10.7[2]/8.5 36.0[3]	9.2/5.4	30	74.8	4	56.1	60.2	179.9	4.4
3	230.6/7.3	3.4/5.6	2.8/2.8	29.0[1]/9.0 10.9[2]/9.0 39.9[3]	9.2/6.0	25	72.7	4	67.8	61.6	180.2	4.7
4	230.7/7.22	3.6/5.5	2.8/2.9	36.7[1]/9.5 15.3[2]/9.5 52.0[3]	9.2/6.2	16	75.0	4	72.8	61.5	184.55	5.7
5	230.9/7.5	3.4/5.6	2.6/3.0	35.2[1]/10.0 17.6[2]/10.0 52.8[3]	9.2/6.2	20	75.3	4	67.0	61.3	183.8	6.3
6	240.8/7.7	6.6/5.5	2.0/3.0	42.3[1]/10.5 17.9[2]/10.5 60.2[3]	9.6/7.2	57	75.0	4	97.4	60.5	158.7	6.3

Amount of lime milk added: [1]In 1st stage; [2]In 2nd stage; [3]Total in both stages.

measurement comprised four series. The results were calculated as a geometrical mean of all individual measurements ($Z_{ite,pan}$). This was also the value of odor concentration in the given sample (c_{od}) expressed in European odor units per m^3 ($ou_E\ m^{-3}$) [25]. Specific odor emissions for tested samples were expressed as SOER [26] (specific odor emission rate, $ou_E\ s^{-1}\ m^{-2}$).

$$\mathrm{SOER} = Q \cdot C \cdot A^{-1} \quad (1)$$

where Q—volumetric flow rate of air in measuring chamber (s^{-1}); C—odor concentration ($ou_e\ m^{-3}$); A—surface of wind tunnel (in this case, it was the surface of samples of pig manure/sediment) for a given odor concentration (c, $ou_E\ m^{-3}$), assumed minimum velocity in measuring chamber = 0.1 m s^{-1} (assumed conditions of so called atmospheric silence) and the surface of samples tested in a laboratory: filtrate—0.063 m^2; sediment—0.046 m^2.

The total odor emission from a pig manure lagoon [22,23] was calculated according to equation:

$$E = C \cdot Q \cdot F \cdot A^{-1} \quad (2)$$

where C—odor concentration (the mean value of three measurements), $ou_E\ m^{-3}$; Q—a volumetric flow rate through device taking samples: 0.0375 $m^3\ s^{-1}$; A—surface of device for taking samples from superficial sources: 0.5 m^2; F—surface of pig manure lagoon: 5,050 m^2.

3. Results and discussion

3.1. Effect of pig manure treatment

The parameters and results of pig manure mineralization and the filtration process allowed for obtaining samples for odor concentration measurements (obtained as described in Section 2.2) are shown in Table 1.

The mineralization process practically eliminated the emission of odors from the filtrate and sediment obtained [22,23]. These resulted from acidification of manure with phosphoric and sulfuric acid. According to [24], emissions could be reduced by acidifying animal manure, which decreases ammonia emissions from slurry in storage and in soil applications. In the study, the manure pH was lowered to 5.5 by adding sulfuric acid. The acidification of the slurry decreased not only NH_3 emissions but also CH_4 and H_2 emissions, consequently, changing the manure characteristics. In [28] pig and cattle slurries were acidified to pH 5.5 before storage. The composition of the slurry after storage indicated that the organic matter turnover during storage was inhibited by acidification, most likely because of the presence of acetate in combination with the low pH values.

The aim of the treatment with mineral acids in the AMAK process was to transform macro-and micro-fertilizer components into forms that are bioavailable to plants by binding volatile organic and inorganic nitrogen compounds and by hydrolyzing the organic matter. Moreover, the addition of acids and superphosphate decreases ammonia emission. Added lime milk solution absorbed also odors at two stages. The addition of a superphosphate also balanced the N and P contents in the sediment and increased the calcium phosphate content in the slurry. The dried sediment contained 40–50% of the amorphous phase and 50–60% of the crystalline phase. The main component of the crystalline phase was hydroxyapatite [19–23].

Table 2 shows characteristics of nutrients and sediments comprised in the tested samples of fertilizers.

Table 2
Nutrients and sediments content in the tested samples of fertilizers produced on the basis of sediment from filtration of treated pig manure [20,23]

Fertilizers produced for	Sediment content (%)	Nutrients ratio in fertilizers $N:P_2O_5:K_2O:MgO$
Beets	48	1:1:1:0.5
Potatoes	56	0.8:1:1:0.3
Corn	48	1:1:1:0.5
Cereals	64	0.4:1:1:0.4

Table 3
Average odor concentration in the samples of gases taken from above the surface of pig manure samples before mineralization, sediments, filtrate and a fertilizer, and in the samples of gases taken from above the surface of pig manure lagoon (sample numbers according to Table 1)

Samples of gases from above the surface of		Average odor concentration ($ou_E\,m^{-3}$)		Specific odor emission SOER ($ou_E\,s^{-1}\,m^{-2}$)			
Raw pig manure		25,047		351.1 (*A*)			
Sample number	Final pH	Filtrate	Sediment	Filtrate (*B*)	*B*/*A* (%)	Sediment (C)	*C*/*A* (%)
Treated pig manure							
1	8.0	8,697	8,556	121.9	34.7	163.7	46.6
2	8.5	5,616	5,724	78.7	22.4	109.5	31.2
3	9.0	1,615	2,315	22.6	6.4	44.3	12.6
4	9.5	648	1,274	9.1	2.6	24.4	6.9
5	10.0	963	333	13.5	3.8	6.4	1.8
6	10.5	216	116	3.0	0.9	2.2	0.6
Fertilizers produced from the sediment							
Samples characteristic		Average odor concentration ($ou_E\,m^{-3}$)		SOER ($ou_E\,s^{-1}\,m^{-2}$) (*D*)		*D*/*A* (%)	
0—raw pig manure		24,712		346.4		98.7	
Fertilizers for	Beets	2,722		38.2		10.9	
	Potatoes	1,413		19.8		5.6	
	Corn	814		11.4		3.2	
	Cereals	756		10.6		3.0	
Pig manure-lagoon odor concentration ($ou_E\,m^{-3}$)							
Pig manure in lagoon	Lagoon—beginning			1,394			
	Lagoon—middle			4,072			
	Lagoon—end			1,375			
	Average			2,280			

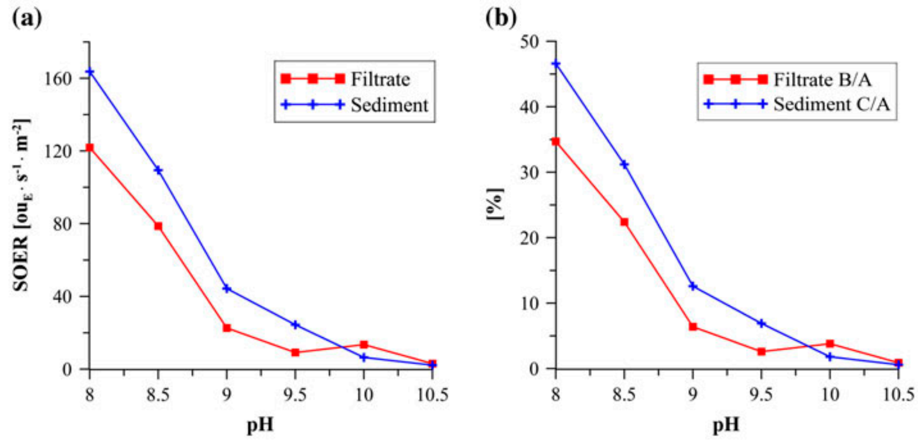

Fig. 1. Relationship between specific odor emission SOER from above surface of filtrate and sediment samples and the final pH value of treated pig manure (a); % reduction of SOER in function of the final pH value of filtrate (b); SOER of the raw pig manure = 100%.

3.2. Effect of pH on odor emission

Table 3 shows average values of odor concentrations determined for laboratory samples (see Table 1) and samples taken from above pig manure lagoon. Estimated specific odor emissions from above the tested samples (SOER, $ou_E\,s^{-1}\,m^{-2}$) were also specified (Figs. 1 and 2).

Relationship between values of odor concentration (along with coefficient of determination R^2) in samples of filtrate and sludge determined upon treatment with an appropriate amount of lime milk causing pH increase after neutralization (specified in Table 3) is shown in Fig. 3.

A significant dependence ($R^2 = 0.98$) between the values of odor concentrations determined for the tested samples of post-filtration sludge and filtrate was confirmed. Basing upon the analyses carried out, significant values of coefficient of determination $R^2 = 0.92$ and 0.97 (for the dependence between pH value and odor concentration determined for samples taken from above filtrate and above sludge, respectively) were found for determined exponential functions (for filtrate samples: $y = 17{,}497e^{-0{,}705x}$ and for sludge samples: $y = 28{,}501e^{-0{,}875x}$).

The test results demonstrated that the most significant parameter affecting intensity of odor emission is the grade of treated pig manure neutralization with

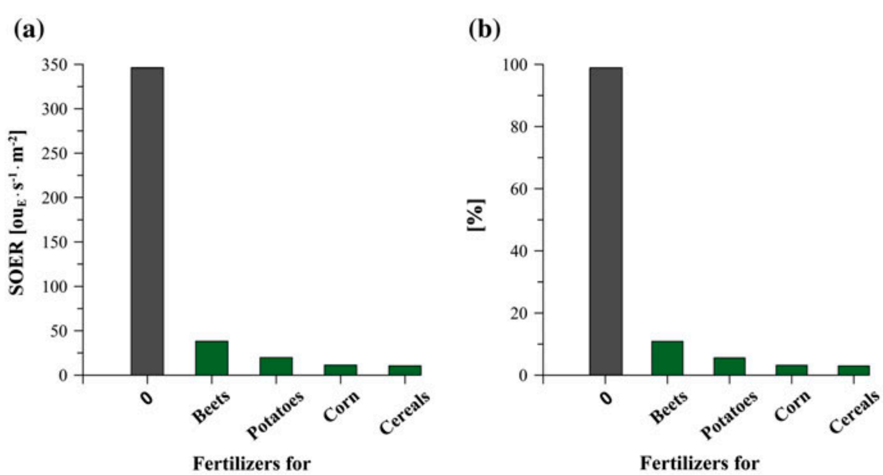

Fig. 2. Relationship between specific odor emission SOER and type of fertilizer produced from sediment after filtration of the treated pig manure (a); % reduction of SOER for various types of fertilizers produced from treated pig manure (b); 0—raw pig manure; SOER of the raw pig manure = 100%.

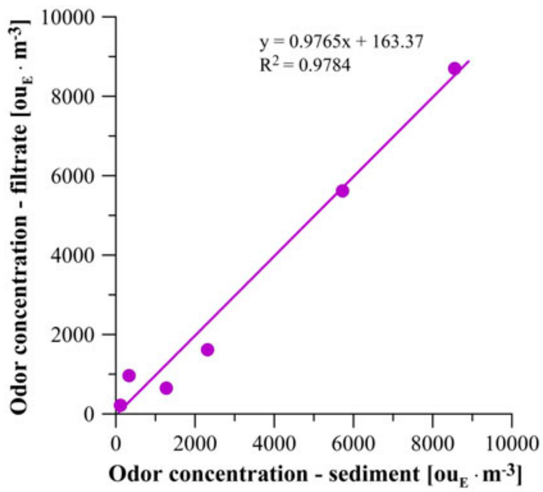

Fig. 3. Relationship between odor concentrations determined for samples taken from above sediment and filtrate.

the use of lime milk. It was found out that an increase in pH value within the range of 8.0–10.5 resulted in reduction of odor concentration from 8,697 to 216 ou_E m^3 and from 8,556 to 116 ou_E m^{-3} for the samples of filtrate and sediment, respectively. Specific odor emission rates also fell down from 129 to 3 ou_E s^{-1} m^{-2} and from 164 to 2 ou_E s^{-1} m^{-2} for the samples of filtrate and sediments, respectively. In the case of tested fertilizer samples, the lowest values of odor concentration and of SOER were found for the sample designated as "Cereals" and amounted to 756 ou_E m^{-3} and 11 ou_E s^{-1} m^{-2}, respectively. For the tested samples of the fertilizer, no dependence between the content of sludge in the samples and the values of odor concentrations obtained was found (standard deviation of ±6%).

The odor concentrations determined for the samples of gases taken from above the pig manure lagoon using dynamic olfactometry and algorithm described in [13,14] made it possible to determine the total odor emission, which amounted to $E = 863{,}676$ ou_e for the lagoon of a surface of 5,050 m^2.

To assess the potential value of the AMAK process, we compared it with other methods for manure treatment in terms of odor elimination. At a piggery in Île d'Orléans, Québec, Canada, the BIOSORTM-Manure biofiltration process [9] eliminated >80% of the odor intensity from the production units and the manure storage. The BIOREK process [29] includes anaerobic digestion, ammonia stripping, ultrafiltration, and reverse osmosis, and its operational costs are high. Ammonia removal efficiencies of up to 99.9% can be obtained at ambient feed temperatures. The SELCO-Ecopurin [30] separation technology has been used for five years on 12 livestock farms in Spain, Italy, and the USA. The high recovery of solids (>90%) makes the use of advanced purification techniques for the liquid an economical alternative. The liquid can be further treated to reduce N and P content in filtrate. The production of methane and energy was affected by the solids concentration and the anaerobic process. The PIGMAN concept [31] reduced the total organic matter, N, and P contents by 96, 88, and 81%, respectively, and practically odor emission. PIGMAN uses simple, inexpensive equipment, and the processed filtrate can be directly spread on agricultural land. The AMAK process, which has also been tested on a pilot scale [19,20,22], has high removal efficiencies for organic matter, N, and P and eliminates the odor intensity of the filtrate and sediment. The treated filtrate can be used to irrigate crops, and the sediment can be used as a mineral–organic fertilizer.

The comparison of the five methods demonstrated that all of the processes had high removal efficiencies for COD, TKN, and P from treated pig manure. Three of the methods (PIGMAN, BIOREK, AMAK) essentially eliminated the odor emissions from the treated products, and four of the methods have been tested at the pilot or field-scale level. The real problems for all methods are the investments in equipment and the processing costs of the pig manure; therefore, only the AMAK process is promising. The advantage of this technology is the possibility of utilizing completely the filtrate and sediment and also eliminating the odor emissions from the filtration products.

4. Conclusions

Odor concentrations in samples of gases taken from above the surface of samples of raw pig manure, the manure treated using the AMAK filtration process, filtrate, sediment from filtration, and fertilizers produced from this sediment as well as in samples of gases taken from above the surface of a pig manure lagoon were determined. The test results demonstrate that the filtration method offers a real possibility of eliminating almost entirely the emission of odors from post-filtration sludge and filtrate.

The tests carried out confirmed that the most significant parameter in the filtration method, which affects intensity of odor emission, is the grade of pig manure neutralization with the use of lime milk. It was found out that an increase in pH value from 8.0 to 10.5 caused a decrease in odor concentration by 99.1 and 99.5% for the samples taken from above the filtrate and the post-filtration sludge, respectively, comparing to the odor concentration found for the samples taken from above raw pig manure. The values of specific odor emission rates were reduced by 99.1 and 99.4% for the samples taken from above the filtrate and the sludge, respectively, comparing to SOER of raw pig manure. In the case of tested fertilizer samples, the lowest values of odor concentration and emission were found for "Cereals"—a designated sample. The odor concentration determined for this sample was lower than its value for the samples taken from above raw pig manure by 97%.

The odor concentration in the samples taken from above the filtrate and post-filtration sludge obtained in the AMAK process was lower than the average odor concentration above pig manure lagoon by 90.5 and 94.5%, respectively.

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