Research Article Open Access

Agnieszka Makara\*, Zygmunt Kowalski, Agnieszka Saeid

# Properties of the filtrate from treatment of pig manure by filtration method

DOI 10.1515/chem-2017-0003 received January 23, 2017; accepted January 30, 2017.

**Abstract:** This paper presents properties of filtrate obtained from pig manure using the AMAK treatment process, which includes the mineralization of macro- and microfertilizer components by the hydrolyzing of organic matter into forms that are bioavailable to plants. Filtration produced two products, sediment and filtrate. The quality of the filtrate allowed for its use as a substitute of water to irrigate crops. Concentrations of heavy metals are very low and therefore the quality of the filtrate fully complies with European standard concerning fertilizers. The used mineralization process practically eliminated odors from the filtrate. The reduction of specific odor emission by 99.1-99.5% in samples taken from above the filtrate, respectively compared to the odor concentration found in samples taken from above raw pig manure. Sediment could be used as raw material for production of mineralorganic fertilizer. Filtrate and filtration sediments analyses show that the majority of nitrogen and other fertilizing compounds included in raw pig manure remains in sediment.

**Keywords:** pig manure, treatment and separation, filtrate properties

#### 1 Introduction

Livestock manures represent a valuable resource, which if used can replace significant amounts of mineral fertilizers [1]. On the other hand, the large volumes of animal manure are not only a source of valuable plant nutrients [2] but

\*Corresponding author: Agnieszka Makara: Institute of Chemistry and Inorganic Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland, E-mail: amak@chemia.pk.edu.pl

Zygmunt Kowalski: Minerals and Energy Economy Research Institute

Polish Academy of Science, Wybickiego 7, 31-261 Cracow, Poland

Agnieszka Saeid: Department of Advanced Material Technologies,

Faculty of Chemistry, Wroclaw University of Technology,

Smoluchowskiego 25, 50-372 Wrocław, Poland

are also a source of air pollution and a threat to aquifers and surface waters [3]. There is a pressing need for the development of technology for management and treatment of animal manure, which can ensure a sustainable use of nutrients and reduce environmental impacts [4-6]. In practice, this is related to significant problems with waste management, which can lead to excess pouring of the manure onto near fields [4]. Stored manure generates odor, primarily due to the anaerobic decomposition of proteins [7].

Manure is treated with the use of various technologies which can be assessed in terms of efficiency by means of the reduction of chemical oxygen demand (COD). Pig slurry is characterized by a high degree of hydration, on average containing 6-8% dry matter, whereas about 70-80% of dry matter comprises organic materials. Due to the domination of chemical transformations in slurry, a more reliable assessment of its organic matter content can be obtained through COD determination. Studies by many authors [4, 7-11] revealed that pig slurry is characterized by a very high biochemical oxygen demand and a rather high chemical oxygen demand [12].

Manure must be separated before it can be treated and utilized [1, 11]. In order to lower the COD parameter of pig manure, the manure is divided into solid and liquid fractions [1]. In a previous study [13], the energy costs to transport liquid manure from its storage site to agricultural fields assuming an annual manure application rate of 81.5 m<sup>3</sup> ha<sup>-1</sup> and a length of 1.8 km for the pipeline running between the storage cisterns and the fields to be treated Under these conditions, the annual was analyzed. energy consumption was between 2726 and 2209 MJ. In comparison, this consumption constitutes 33% and 27% of the energy costs of nitrogen from anhydrous ammonia and urea, respectively. The resulting increase in manure transport costs for farmers in pig-dense regions, along with the potential of surface and groundwater pollution from the land spreading of manure, has resulted in the need for practical and economical on-farm solutions for pig manure treatment.

Many pig slurry separation techniques influence the characteristics of N in the resulting liquid and solid fractions [11, 14]. The separation of manure produces a solid fraction and a liquid fraction. The solid fraction can be applied to fields as a fertilizer, composted, or used as a fuel. The liquid fraction may be irrigated, or it could be treated further. Methods of slurry separation include: sedimentation, filtration and mechanical methods. Efficient separation usually requires the use of chemical additives to the slurry to encourage the binding or smaller particles before separation begins [1, 11, 14].

The example of using the integrated manure treatment systems is a SELCO-Ecopurin separation method [15] which has been introduced in swine farms in Europe and the USA. SELCO-Ecopurin is a technique of dividing manure into solid and liquid fraction by the use of polyacrylamide flocculants and further filtration with a filtration press and pressure flotation machine. The average efficiency of the separation process in relation to the reduction of COD is equal 63-84%. After the second stage of treatment (further separation with polyacrylamide addition), a considerable reduction of COD occurs (97% with the starting level to 60 g L<sup>-1</sup>).

The BIOSORTM-Manure biofiltration process [4] for pig manure treatment makes it possible to obtain the overall pollutant removal: more than 95% of BOD, more than 97% of suspended solids SS, more than 84% of TKN, as well more than 87% of P, despite strong variability in BOD, (10-20 g L-1), SS (10-20 g L-1), TKN (2.0-3.8 g L-1), and P (0.5-0.9 g  $L^{-1}$ ). This process eliminated > 80% of the odor intensity from the production units and the manure storage.

In the final scheme of the PIGMAN concept that was performed on a laboratory scale [16], the following successive process steps was used: thermophilic anaerobic digestion with sequential separation by decanter centrifugation, post-digestion in an up flow anaerobic sludge blanket (UASB) reactor, partial oxidation, and finally the oxygen-limited autotrophic nitrification-denitrification (OLAND) process. This combination of mentioned steps effected in reduction of the COD, nitrogen, as well as phosphorus content in filtrate by 96%, 88%, and 81%, respectively.

The BIOREK process [17], which has been tested on a pilot scale, includes anaerobic digestion, ammonia stripping, ultrafiltration, and reverse osmosis, and its operational costs are high. That technology retains biomass. High, up to 99.9% of ammonia removal efficiencies can be obtained at ambient feed temperatures.

In the past few years, utilization of a membrane process in separation has been improved [17-19]. In order to lower the manure COD in [18], the manure was divided into fractions by the use of a filter press, or hydrocyclone,

or vibrating screen or screw press. In the second stage, liquid fraction was treated on a bag filter (up to ~15 g L<sup>-1</sup> COD) and then microfiltration was applied and reverse osmosis. The content of the COD in the obtained permeate was 0.2 g L<sup>1</sup>. The liquid fraction obtained can be used to irrigate fields or discharged into public sewage system, while the solid fraction can be used as a fertilizer or a renewable source of energy [18]. The work [19] integrated whirling and ultrafiltration system enabled to lower the COD content from 62.8 to 28.0 g L<sup>-1</sup>.

The presented paper examined the properties of the filtrate obtained from pig manure treated by the elaborated complex pig manure treatment technology [20, 21, 22] (AMAK process). The treatment of pig manure by mineral acids in the AMAK process aims to mineralize the macro- and microfertilizer components into forms that are bioavailable to plants by binding volatile organic and inorganic nitrogen compounds and by hydrolyzing organic matter. Moreover, the addition of acids and the alkalization of the manure slurry with lime milk at two stages of the treatment process resulted in the elimination of pathogens. The addition of a superphosphate influences the balance of the content of N and P in the sediment and increased the calcium phosphate content in the slurry. Manure processing produced two products, i.e. filtration sediment and filtrate. Sediment can be used as a raw material for the production of mineral-organic fertilizer [23, 24], while the physicochemical properties of the filtrate were analyzed in terms its use as a substitute of water for sprinkling fields or treat it in classic sewage treatment plants.

# 2 Experimental Procedure

#### 2.1 Characteristics of pig manure

The pig manure was taken from a piggery located near the town of Piła, northern Poland that produces piglets intended for fattening in other pig farms as well as sows for renewing the flock. The average monthly livestock statistics as to the type of animals were as follows: 1101 sows, 64 gilts, 2536 sucking piglets, 140 weaned piglets, 200 shoats, 160 porkers, in total 4201 [8, 25]. Pig manure samples were taken from drain pipe carrying slurry from a piggery to a lagoon. Each time sampling was made using the same system and source of sample [8, 9, 20]. For the treatment process, representative 10 L samples of pig manure taken were used and a total of 150-230 g of manure was processed in one batch.

#### 2.2 Analyses

The chemical composition of the pig manure was determined in accordance with the Polish standards for the examination of waste, wastewater, and fertilizer. In the sample taken, the content of nitrogen, chemical oxygen demand, phosphorus, potassium, calcium and dry mass was determined according to Polish standards [26-32]. The microbiological analyses were conducted in accordance with Polish standard [33] to identify the bacilli of genus Salmonella and live eggs of parasites.

For laboratory tests, a pressure filter of volumetric capacity of 2000 mL manufactured by Sartorius was used for manure filtration. The Kjeldahl's method for the nitrogen determination in the manure and in the filtrate, DK6 mineralizer and equipment for distillation with steam (manufactured by VELP), were used. The phosphorus content was determined with a Nanocolor UV/VIS spectrophotometer (manufactured by Macherey-Nagel). For COD determination samples were mineralized with a M-9 mineralizer. To determine the Ca. K. Mg. P. and S content in the sediment, an inductively coupled plasma atomic emission (ICP-AE) spectrometer (OPTIMA 7300 DV manufactured by Perkin Elmer) was used. The C, H and N contents were determined using a Perkin Elmer PE 2400 analyzer. The content of macroelements (Ca, Mg, S, Al), heavy metals (As, Pb, Cd, Cr, Ni) and microelements (Cu, Zn, Mo, Fe, Mn) were determined using Inductively Coupled Plasma Atomic Emission (ICP-AE) spectrometer of OPTIMA 7300 DV (manufactured by Perkin Elmer). The content of potassium and calcium was determined with flame atomic absorption spectroscopy (FAAS), using an OPTIMA 7300 DV apparatus (manufactured by Perkin Elmer). The concentration of mercury (Hg) was determined with atomic absorption spectroscopy method, by means mercury analyzer AMA-254 ALTEC.

According to the Directive on fertilizers, chemical analyses of fertilizers includes the determination of [24]:

- the total content of phosphorus compounds with the use of the method of extraction of phosphorus contained in the fertilizer with a mixture of nitric and sulfuric acid.
- the content of phosphorus compounds soluble in formic acid with the use of the method of determination of extracted phosphorus soluble in 2% formic acid,
- the content of phosphorus compounds soluble in citric acid with the use of the method of determination of extracted phosphorus soluble in 2% citric acid,
- the content of phosphorus compounds soluble in ammonium citrate with the use of the method of deter-

mination of extracted phosphorus soluble in inert ammonium citrate in temperature of 65 °C (pH = 7).

The total content of nitrogen was determined by the use of the method involving the reduction of nitrates to ammonia in an acidic environment in the presence of powdered chrome and distilling the ammonia off the alkaline solution [26]. In a study [28], this method was used to determine the Kjeldhal nitrogen in the sample. Ammonia nitrogen was analyzed by the distillation method with end acid-base titration in accordance with the Polish standard [29]. K<sub>3</sub>O analyses were performed with the use of the flame atomic absorption spectrometry in accordance with the standard [32]. The calcium content was determined (on a previously mineralized sample) in accordance with [24]. To compare the emission of odors from raw manure and products of its treatment and filtration, gases sampled from the raw pig manure before treatment and from the filtrates and sediments after treatment were measured using the dynamic olfactometric method [34-36]. The odor concentrations in the given sample were compared by (c<sub>st</sub>) expressed in European Odor Units per m<sup>3</sup> (ou<sub>r</sub> m<sup>-3</sup>) [34] and specific odor emissions expressed as SOER [36] (Specific Odor Emission Rate, ou, s-1 m-2):

$$SOER = Q \cdot C \cdot A^{-1} \tag{1}$$

where: Q - volumetric flow rate of air in measuring chamber (s<sup>-1</sup>); C – odor concentration (ou<sub>E</sub> m<sup>-3</sup>); A – surface of wind tunnel (in this case it was a surface of samples of pig manure/filtrate) for a given odor concentration (c, ou<sub>r</sub> m<sup>-3</sup>).

#### 2.3 Calculations

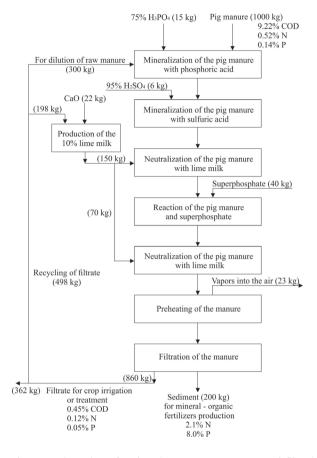
The correlation coefficients were obtained by Statistica software vers. 12.0. Correlation was considered statistically significant at  $\alpha$  < 0.05.

#### 3 Results and Discussion

The physicochemical characteristics of the raw pig manure and filtrate are presented in Table 1. The chemical oxygen demand (COD) value varied within a range of 9-113 g L-1, whereas the biochemical oxygen demand (BOD) value varied within a range of 2.6-41 g L<sup>-1</sup> [12]. As it was observed, the results of chemical and biochemical oxygen demands are closely related with the dry matter content in the manure and their values increase along with dry matter [25]. BOD as well as COD was statistically correlated with dry matter, r=0.835 (p<0.05) and 0.856 (p<0.05), respectively. The content of fertilizer components also varies, and the amount of dry matter varied within a range of 10-95 g L<sup>-1</sup> and 1-7 g L<sup>-1</sup> in the case of the content of potassium. Kjeldahl nitrogen was characterized with values within a range of 3-9 g L<sup>-1</sup>. Microbiological research did not indicate any presence of Salmonella or live parasite ova. The chemical composition of manure indicates very strong fluctuations and is the primary challenge with manure processing [1, 11]. The major differences in composition of the manure are dependent on the methods of collection, dilution, and storage. There is significant difference in the composition of pig slurry from different categories of pigs related to different diets [37]. Recent advances in reproductive efficiency also have led to less manure generated from sows and boars as a percent of the total waste stream. Thus, previous estimates of waste production and composition may prove to be inaccurate estimators and in many cases will overestimate both the total volume of production and the composition of the pig manure produced [1, 11].

The sample of filtrate was prepared according to the new pig manure treatment and filtration AMAK process [22]. The flow sheet of the AMAK process is presented in Figure 1. Approximately 75% phosphoric acid and 95% sulfuric acid were added to the raw pig manure to obtain pH values of 5.5 and 3.0, respectively. The slurry was then treated with a 10% solution of lime milk to obtain a pH of ~10.5. Afterwards superphosphate was added up to 4% of the raw manure weight, and the second alkalization step by addition of lime milk to obtain a pH of 10.5. The processed slurry was heated up to 90°C and filtered with the pressure filter. As a result of filtration, light straw colored filtrates, were obtained.

The advantage of worked out technology is the method of incorporation in organic phase of the manure of 40-59% of crystalline phase. All these resulted in high filtration rate with used pressure filters over 1000 L m  $^2$  h $^1$  and good quality of filtrate [8, 20, 22]. According to several



**Figure 1:** Flow sheet for the pig manure treatment and filtration process (AMAK process).

Table 1: Physicochemical characteristics of tested pig manure and filtrate obtained.

Sample	Concentration in raw manure Rm and filtrate F [g L¹] and removal efficiency RE in [%]													
	DM*	K		Ca		N			COD			P		
	Rm	Rm	F	Rm	F	Rm	F	RE	Rm	F	RE	Rm	F	RE
1	94.8	6.59	3.05	2.18	1.95	7.97	1.67	79.0	98.30	4.42	95.5	1.81	0.07	96.1
2	10.0	1.18	1.15	0.23	0.19	2.96	0.59	80.0	8.76	0.44	95.0	0.22	0.01	96.5
3	17.0	1.16	1.08	0.57	0.61	3.96	0.77	80.5	36.88	3.90	95.3	0.78	0.02	97.0
4	80.0	2.27	2.00	1.88	1.75	9.18	1.76	80.8	60.90	3.11	94.9	1.77	0.06	96.8
5	82.4	2.22	2.31	2.27	2.31	6.31	1.27	79.9	112.80	5.53	95.1	1.59	0.06	96.0
6	39.0	1.00	0.95	1.54	1.62	4.31	0.86	80.1	23.65	1.09	95.4	0.79	0.03	96.6
7	60.2	1.43	1.25	1.98	1.87	4.40	0.90	80.6	38.60	4.13	96.0	0.83	0.03	96.9

DM\*- dry matter; We did not detect *Salmonella* group bacilli (amount L¹) or parasite eggs (*Ascaris* sp., *Trichuris* sp., *Toxocara* sp.) (amount L¹) in any samples; DM content in the filtrate was not detected in any samples.

studies [1, 22, 23], the obtained sediment containing high quantities of bio-available calcium phosphates could be used as a semi-product to obtain a mineral-organic fertilizer containing nitrogen, phosphorus, potassium, calcium, and sulfur compounds and microelements. Simultaneously the filtrate was recycled to prepare the lime milk solution, and eventually, to dilute the raw pig manure. The remaining filtrate could be used to irrigate crops or could be treated in conventional biological wastewater treatment plants [20, 22].

## Obtaining filtrate with controlled quality parameters

To obtain a high-quality filtrate, the pig manure treatment process should be properly controlled. The influence of the total solids content in raw pig manure, and the quantity of superphosphate as well as the addition of lime milk during the process, on the resultant concentrations of COD, N, as well as the P in the produced filtrate were examined [8, 22]. The results showed that these parameters can be regulated in the pig manure treatment process to obtain a filtrate with proper quality. To produce a filtrate with the optimal quality, the treated manure should contain 4-5% TS. The quantity of superphosphate added to the manure should be equal to 4% of the weight of the raw pig manure, while the quantity of lime milk added to the manure should increase the pH of the neutralized manure up to 10.5.

Table 1 includes comparisons between COD content in manure and filtrate obtained as a result of use of the pig manure treatment and filtration AMAK process. Calculations of the removal of COD, N, and P were made on the basis of the mass balances given the mass and volume of the effluents and the concentration of COD, N, and P in the effluents and in the raw pig manure. The removal efficiency RE (%) was calculated according to the equation (2):

$$RE = (C_A - C_B) / C_A \times 100 \tag{2}$$

where  $C_{\Delta}$  is the concentration in [g L<sup>-1</sup>] of the COD, N, and P in the sample of raw pig manure and C<sub>R</sub> is the concentration in [g L<sup>1</sup>] of the COD, N, and P in the filtrate.

#### Chemical composition of the treated filtrate

With the intention of utilizing the filtrate as a fertilizer, the content of the fertilizer components in filtrate was determined. Table 1 presents the summary of the contents in the liquid phase extracted from manure, the Kjeldajhl nitrogen, phosphorus, potassium and total content of calcium. The average content of the total nitrogen varied within a range of 0.17 - 0.59%, and within a range of 0.09- 0.42% for ammonium nitrogen. The varying nitrogen content is the result of a diverse chemical composition of the raw pig manure.

Despite the strong variability in COD (9-113 g L<sup>-1</sup>), N (3-9 g  $L^{-1}$ ), and P (0.2-1.8 g  $L^{-1}$ ) values in raw pig manure, the removal efficiencies were high, 95-96% for COD, up to 80% for TKN, and 96-97% for P. Statistically significant correlation were found between the COD, N and TKN for manure and filtrate, r=0.888 (p<0.05), r=0.995 (p<0.05) and r=0.982 (p<0.05), respectively.

Amount of phosphates in a form of soluble phosphorus in filtrate expressed as P<sub>2</sub>O<sub>5</sub> was determined in accordance with analytical research enabling to estimate its content in digestible forms (Table 2). The filtrate could be used to irrigate crops and these values are interesting from these terms [20, 22]. The bioavailability of phosphorus was examined in accordance with [24].

The content of microelements and heavy metals in the filtrate were summarized in Table 3. The microelement content in filtrate was low. The highest content was that of potassium and its level varied within a range of 1040 -2310 mg L<sup>1</sup>. The contents of sulfur and iron in filtrates vary between 68 - 424 mg L<sup>-1</sup> and 2.9 - 185 mg L<sup>-1</sup> respectively. Concentrations of heavy metals are very low and therefore the quality of the filtrate fully complies with the European standard concerning fertilizers [24].

Table 4 shows also content of fertilizing compounds in filtration sediment. Studies assessing the bioavailability of phosphate form in the sediment were made in terms their use as the fertilizer [20, 22, 23]. Table 5 shows the results of analyzes of microelements and heavy metals in filtration sediment.

Most of nitrogen compounds present in the manure remains in filtration sediment [8]. The particle sizes in the slurry are important for evaluation of sedimentation during storage and slurry separation, e.g. filtration to retain particles above a certain size. The amount of DM in the fraction <0.025 mm is larger in pig slurry than in cattle slurry, 66-70% and 50-55% of DM is in the particlesize fraction smaller than 0.025 mm in respectively pig and cattle slurry. Anaerobic digestion reduces DM concentration of animal slurry, and changes the partitioning between fraction of large and small particles. It has been observed that particles < 10 µm accounts for 64% of DM in raw slurry, while it increases to 84% of DM in anaerobically digested slurry [1].

**Table 2:** Content of phosphates in filtrate in digestible forms.

P form soluble in:	[g L¹] in filtrate sample									
	1	2	3	4	5	6	7	Average		
mixture of mineral acids HNO <sub>3</sub> :H <sub>2</sub> SO <sub>4</sub>	0.09	0.05	0.07	0.08	0.07	0.07	0.07	0.07		
2% citric acid	0.04	0.02	0.02	0.03	0.02	0.03	0.03	0.03		
2% formic acid	0.03	0.02	0.02	0.03	0.02	0.03	0.03	0.03		
ammonium citrate solution	0.06	0.04	0.04	0.05	0.04	0.06	0.06	0.05		
water	0.04	0.02	0.03	0.04	0.03	0.03	0.03	0.03		

**Table 3:** Content of microelements and heavy metals in filtrate.

Element	Content in filtrate [mg L¹] (SD for duplicate analysis)									
	1	2	3	5	6					
As	<0.01	<0.01	0.021±0.004	0.067±0.013	0.056±0.011					
В	3.7±0.6	3.4±0.5	1.7±0.3	1.7±0.3	4.1±0.6					
Cd	0.0074±0.0015	0.0016±0.0003	0.00060±0.00012	0.00058±0.00012	0.016±0.003					
Cr	0.12±0.02	0.011±0.002	0.017±0.003	0.014±0.003	0.33±0.05					
Cu	3.2±0.5	0.70±0.10	0.27±0.04	0.24±0.04	7.8±1.2					
Fe	41±6	6.9±1.0	3.3±0.5	2.9±0.4	185±28					
Hg	0.0025±0.0004	0.00064±0.0001	0.00056±0.0001	0.00078±0.00010	0.0017±0.0002					
K	2310±460	1040±210	1070±210	1040±210	1910±380					
Mn	8.0±1.2	0.46±0.2	0.56±0.08	0.44±0.070	25±4					
Мо	0.084±0.02	0.057±0.011	0.014±0.003	0.0091±0.0018	0.14±0.02					
Ni	0.20±0.003	0.036±0.007	0.077±0.015	0.024±0.005	0.29±0.04					
Pb	0.077±0.15	0.0092±0.0018	0.029±0.006	0.0086±0.0017	0.40±0.06					
S	225±34	208±31	69±10	68±10	424±64					
Zn	16±2	2.4±0.4	0.96±0.14	0.81±0.12	41±6					

 Table 4: Content of fertilizing compounds in the filtration sediment.

Compound	Content i	Average	SD					
	1	2	3	4	5	6	value	
N <sub>total</sub>	0.45	0.51	0.45	0.23	0.23	0.32	0.37	0.12
N <sub>ammonium</sub>	0.21	0.22	0.21	0.25	0.25	0.19	0.22	0.024
P form (as P <sub>2</sub> O <sub>5</sub> )soluble in:								
- mixture of mineral acids HNO <sub>3</sub> :H <sub>2</sub> SO <sub>4</sub>	13.92	13.54	18.32	9.98	8.37	10.33	12.41	3.61
- 2% citric acid	4.77	5.20	5.71	4.52	4.20	5.43	4.97	0.57
- 2% formic acid	6.46	6.30	6.37	5.45	4.94	6.29	5.97	0.63
- ammonium citrate solution	3.21	3.26	3.43	1.52	3.17	3.92	3.09	0.81
- water	0.77	0.35	0.50	0.54	0.31	0.61	0.51	0.17
K <sub>2</sub> O	0.17	0.14	0.17	0.21	0.21	0.17	0.18	0.027
CaO	20.8	9.61	16.13	11.0	16.4	17.32	15.21	4.17
S	0.77	0.82	0.98	0.84	1.05	NA	0.88	0.18

NA - not analysed

**Table 5:** Content of microelements and heavy metals in the filtration sediment.

Element	Conte [mg k	nt in the	Average SD value				
	1	2	3	4	5		
В	26	23	22	28	24	25	2.4
Cu	32	42	37	22	24	31	8.5
Fe	884	892	980	742	880	876	85
Mn	86	97	80	77	65	81	12
Mo	0.77	0.89	0.95	0.76	0.50	0.77	0.17
Zn	186	216	218	155	130	181	38
As	5.5	4.5	7.0	5.6	3.6	5.2	1.3
Cr	50	52	71	36	32	48.2	8.0
Ni	4.6	3.5	4.4	3.2	3.1	3.8	0.63
Cd	2.6	2.6	3.4	2.0	1.7	2.5	0.65
Hg	0.02	0.018	0.027	0.015	0.016	0.019	0.0048
Pb	1.4	1.1	1.7	1.0	1.7	1.4	0.33

Table 6: Average odor concentration in the samples of gases taken from above the surface of pig manure samples before mineralization and treated filtrate.

Samples of gases from above the surface of	Average odor concentration (ou <sub>E</sub> m <sup>-3</sup> )	Specific odor emission SOER (ou <sub>E</sub> s <sup>-1</sup> m <sup>-2</sup> )	B/A(%)
Raw pig manure	25047	351.1 (A)	
Filtrate samples			
1	310	2.3 (B)	0.7
2	290	3.3 (B)	1.1
3	265	2.7 (B)	1.0
4	255	1.6 (B)	0.6
5	270	2.2 (B)	0.8
6	216	1.9 (B)	0.9

More than 80% of N and P is in the fraction < 0.125 mm of cattle slurry [38] and analysis of particle size fraction showed that in slurry more than ca. 70% of the un-dissolved N and P was in the particle size fraction 0.45-250 µm. A proper method of filtration yielded good quality filtrate and these resulted in increased content of N in filtration sediment.

Concentrations of heavy metals are low and therefore quality of the filtration sediment complies with European standard concerning fertilizers [24].

#### Elimination of odors emission

The emission of odors is very inconvenient during swine manure storage in lagoons [1, 8]. A reduction of emissions of ammonia from slurry in storage as well as from soil applications can be achieved through acidification of animal manure [39, 40]. The composition of the slurry after storage indicated that organic matter was inhibited by acidification during the storage, most likely because of the presence of acetate in the combination with the low pH values [40].

The utilization of the mineralization process practically eliminated the emission of odors from the filtrate and sediment (Table 6) [22, 34, 36]. Even after 3 months, odor emissions from the filtrates [34, 36] were not detected. The reduction of the specific odor emission and odor concentration by 99.1% and 99.5% in samples taken from above the filtrate, respectively, as compared to the odor concentration found in samples taken from raw pig manure referred to above.

#### 4 Conclusions

This paper presents research results on the quality of filtrate generated as a result of the use of elaborated complex pig manure treatment technology (AMAK process) and provides a new solution for the treatment and filtration of pig manure. Manure filtration produces two products, filtrate and filtration sediment. The presented physicochemical properties of the filtrate were analyzed in terms its use as a substitute of water for sprinkling fields. The properties of the filtrate supports its use as a substitute of water for to irrigate crops. Concentrations of heavy metals are very low and therefore quality of the filtrate fully complies with European standard concerning fertilizers. The mineralization process practically eliminated the emission of odors from the filtrate. A reduction of specific odor emission odor concentration was by 99.1-99.5% in samples taken from above the filtrate, respectively comparing to the odor concentration found in samples taken from above raw pig manure.

Sediment could be used as raw material for production of mineral-organic fertilizer. Filtrate and filtration sediments analyses show that the majority of nitrogen and other fertilizing compounds included in pig manure remains in sediment.

Acknowledgements: This study was conducted within the framework of the Development Project No. 14-0003-10/2010, supported by a grant from the National Center for Research and Development.

### References

- [1] Sommer S.G., Christensen K.V., Jensen L.S., Environmental Technology for Treatment and Management of Bio-waste. Compedium. University of Southern Denmark, Faculty of Engineering, Institute of Chemical Engineering, Biotechnology and Environmental Engineering & University of Copenhagen, Faculty of Life Science, Plant and Soil Science Laboratory, Department of Agricultural Sciences, 2009.
- [2] Bouwman, A.F., and Booij, H., Global use and trade of foodstuffs and consequences for the nitrogen cycle, Nutr. Cycl. Agroecosys., 1998, 52, 261-26.
- [3] Steinfeld H., Gerber P., Wassenaar, T., Castel V., Rosales M., de Haan C., Livestock long shadow - Environmental issues and options. FAO - Rome, 2006.
- [4] Buelna G., Dubé R., Turgeon N., Pig manure treatment by organic bed biofiltration, Desalin., 2008, 231, 297-304.
- Imbeah M., Composting piggery waste: A review, Bioresour. Technol., 1998, 63, 197-203.
- Rulkens W.H., Klapwijk A., Willersb H.C., Recovery of valuable nitrogen compounds from agricultural liquid wastes: potential possibilities, bottlenecks and future technological challenges, Environ. Pollut., 1998, 102 S1, 727-735.
- De la Torre A.I., Jimenez J.A., Carballo M., Fernandez C., Roset J., Munoz J., Ecotoxicological evaluation of pig slurry, Chemosphere 2000, 41, 1629-1635.
- Makara, A., Kowalski, Z., Innovative bio-products for agriculture: Pig manure utilization and treatment, Nova Science Publishers, Inc., New York 2016.
- [9] Kowalski Z., Makara A., Fijorek K., Changes in the properties of pig manure slurry, Acta Biochim. Pol., 2013, 4, 845-850.
- [10] Konieczny K., Kwiecińska A., Recovery of water from swine manure - laboratory research results, Ecol. Eng., 2011, 24, 81-88.
- [11] Hjorth M., Christensen K.V., Christensen M.L., Sommer S.G., Solid-liquid separation of animal slurry in theory and practice: A review, Agron. Sustain. Dev., 2010, 30, 153-180.
- [12] Marszałek M., Kowalski Z., Makara A., Physicochemical and microbiological characteristics of pig slurry, Technical Transactions, Chemistry 1-Ch, 2014, 81-91.
- [13] Wiens M.J., Entz M.H., Wilson C., Ominski K.H., Energy requirements for transport and surface application of liquid pig manure in Manitoba, Canada, Agric. Syst., 2008, 98, 74-81.
- [14] Fangueiro D., Gusmao M., Grilo J., Porfirio G., Vasconcelos E., Cabral F., Proportion, composition and potential N mineralisation of particle size fractions obtained by mechanical separation of animal slurry, Biosystems Eng., 2010, 106, 333-337.
- [15] Martinez-Almela J., Barrera J.M., SELCO-Ecopurin pig slurry treatment system, Bioresour. Technol., 2005, 96, 223-228.
- [16] Karakashev D., Schmidt J.E., Angelidaki I., Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure, Water Res., 2008, 42, 4083-4090.

- [17] Du Preez J., Norddahl B., Christensen K., The BIOREK® concept: a hybrid membrane bioreactor concept for very strong wastewater, Desalin., 2005, 183, 407-415.
- [18] Pieters J.G., Neukermans G.G.J., Colanbeen M.B.A., Farm-scale membrane filtration of sow slurry, J. Agric. Engng Res., 1999, 73, 403-409,
- [19] Konieczny K., Kwiecińska A., Recovery of water from swine manure - laboratory research results, Ecol. Eng., 2011, 24,
- [20] Kowalski Z, Makara A., Matýsek D., Hoffmann J., Hoffmann K., Pig manure treatment by filtration, Acta Biochim. Pol., 2013, 4, 839-844.
- [21] Kowalski Z., Makara A., Hoffmann J., Hoffmann K., Method for treatment of pig manure slurry, Polish patent 220702, 2015.
- [22] Makara, A., Kowalski, Z., Pig manure treatment and purification by filtration, J. Environ. Manage., 2015, 161, 317-324.
- [23] Hoffmann K., Huculak-Maczka M., Popławski D., Makara A., Kowalski Z., Hoffmann J., Skut J., Mineral-organic fertilizers based on filter sludge from pig slurry treatment, Przem. Chem., 2013, 92, 1145-1149, (in Polish).
- [24] Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October. 2003 relating to fertilisers.
- [25] Kowalski Z., Makara A., Fijorek K., Changes in the properties of pig manure slurry, Acta Biochim. Pol., 2013, 4, 845-850.
- [26] PN-Z-15011-3:2001, Municipal waste compost Determination of: pH, content of organic substance, organic carbon, nitrogen, phosphorus and potassium.
- [27] PN 93/C-87085, Fertilizers Determination of total nitrogen content with distillation method.
- [28] PN-EN 25663:2001, Water quality. Determination of Kjeldahl nitrogen. Method after mineralization with selenium. Kjeldahl method of determination of nitrogen.
- [29] PN-75/C-04576/15, Determination of ammonium nitrogen in sewage sediments.
- [30] PN-EN 1899-1:2002, Water quality Determination of the biochemical oxygen demand after n days (BOD).
- [31] PN-ISO 6060:2006, Water quality Determination of the chemical oxygen demand.
- [32] PN-ISO 9964-2:1994, Water quality Determination of sodium and potassium - Part 2: Determination of potassium by atomic absorption spectrometry.
- [33] PN-EN ISO 6579:2003, Microbiology of food and animal feeding stuffs - Horizontal method for the detection of Salmonella spp.
- [34] Sówka I., Kowalski Z., Skrętowicz M., Makara A., Sobczyński P., Stokłosa K., Use of field inspections and inverse distance weighted method to assess the odor impact of a selected pig farm, Przem. Chem., 2013, 92, 1169-1172, (in Polish).
- [35] PN-EN:13725:2007, Air quality Determination of odor concentration by dynamic olfactometry.
- [36] Makara A., Kowalski Z., Sówka I., Possibility to eliminate emission of odor from pig manure treated using AMAK filtration method. Desalin. Water Treat., 2016, 57, 1543-1551.
- [37] Sanchez M., Gonzales J.L., The fertilizer value of pig slurry. I. Values depending on the type of operation, Bioresour. Technol., 2005, 96, 1117-1123.
- [38] Mayer M., Cost effective solutions with partial stream digestion, In Proceedings of ECN/ORBIT e.V. Workshop 2008, The Future for Anaerobic Digestion of Organic Waste in Europe, Weimar, Germany.

- [39] Petersen S.O., Andersen A.J., Eriksen J., Effects of cattle slurry acidification on ammonia and methane evolution during storage, J. Environ. Qual., 2012, 41, 88-94.
- [40] Sørensen P., Eriksen J., Effects of slurry acidification with sulphuric acid combined with aeration on the turnover and plant availability of nitrogen, Agric. Ecosyst. Environ., 2009, 131, 240-246.