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Research Article

The Influence of Different Chemical Methods of Pig Manure Treatment on the Emission of Odor-Forming Substances

Alexander A. Ratko*, Yuliya V. Duko, Vyacheslav V. Shevchuk

Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, 9/1, Surganova Street, 220072, Minsk, Belarus

***Corresponding Author:** Alexander A. Ratko, Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, 9/1, Surganova Street, 220072, Minsk, Belarus

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Abstract.

Background: The research on optimal composition of chemical reagents for deodorization and disinfection of liquid manure slurry of pig breeding complex facility was performed.

Results: It was established, that all three compositions (sulfuric acid combined with sodium hypochlorite, ammonium persulphate in combination with peracetic acid, and also the mixture of sodium nitrite and ammonium molybdate) provide the removal of unpleasant odors, however, more preferable from the point of preservation of disinfecting effect, are the mixtures containing ammonium persulphate plus peracetic acid and sodium nitrite combined with ammonium molybdate (high deodorizing and disinfecting effect was observed after 21 days).

Conclusion: Manure mixtures obtained as a result of such treatment are harmless for the environment and could be used as a main component of organo-mineral fertilizers.

Keywords: emission of gases; manure odor; disinfection; deodoration; environmental chemistry; environmental toxicology; air quality

Introduction

One of the most common problems of modern pig-breeding is the presence of unpleasant odor of manure slurries of livestock complex. As it is known, the manure, that is formed as a result of animals breeding, is traditionally collected and stored in spacious artificial lagoons – manure storages, where after 12 months (on the average) it loses its harmful properties and gradually turns into a fertilizer, the latter is afterwards taken out to the fields. During the entire storage time of manure, substantial quantity of volatile organic compounds is released into the air, they possess intensive unpleasant odor and are harmful for the humans and animals. Additional factors of pollution of atmospheric air by unpleasant odors are ventilation, aeration lights – sources of emissions from pigsties.

Characteristic smell of pig manure is formed as a result of bacterial activity. Odor-forming substances are the final or intermediate products of fermentation decomposition of feces by anaerobic bacteria [1]. It is known that the features of the odor of pig manure are reasoned by the presence of approximately 40 compounds that are related to 14 chemical classes, amongst them the basic are volatile organic acids, sulphur compounds, aromatic compounds (indole, scatole, phenol-, p-cresole), aldehydes (formaldehyde, acetaldehyde, butanal) [2].

The remarkable feature of air pollution by odor-forming substances is that the presence of the latter even on the level of lower than limiting acceptable values causes irritation, discomfort and deterioration of health. This is connected with lower value of the limit of feeling of odor-forming substances than their limiting acceptable concentrations in atmospheric air [3].

Latest trend to the increase of the number of pigs on livestock complex made the problem of unpleasant odor the center of attention of the community. The problem of processing and utilization of wastes of pig-breeding is exceptionally actual for many countries of the world, including the Republic of Belarus. There is strong necessity in the effective methods of control of odors, that are generated by pig breeding facilities. Different approaches have been developed by the specialists of various countries to solve his problem - neutralization, masking, bonding, oxidation or decreasing the emission of unpleasant odors of pig farms by using chemical or microbiological reagents, technical means of air purification using bio-filters. One of the most widely used means of treatment of manure slurry is the method of oxidation, where the substances, responsible for odor pollution of the atmosphere, are effectively decomposed [4].

The units of air purification in industrial facilities on the basis of bio-filters did not get wide practical usage due to their high cost, high energy consumption, complexities in exploitation. The use of such units at pig breeding facilities leads to the increase of the cost and decrease of competitiveness of the product.

There are several studies on the use of chemical reagents for removal of unpleasant odors, they use hydrogen peroxide, potassium permanganate, ozone, iron compounds and etc. [5-7]. Indeed, laboratory studies demonstrate 90% effectiveness of the use of such methods, however, such methods are not realized on industrial scale due to the difficulties occurring as a result of changing composition of manure slurries and strong influence of weather factors on the conditions of deodorizing measures. Besides, reagents for de-odorizing of manure slurries have limited time of action, therefore, the necessity to repeat the treatment of the manure often occurs [8]. There is little data in the literature on the use of microbiological reagents - inhibitors of microbiological activity of the bacteria, responsible for the emission of odor-forming substances [9], the means of their use are not sufficiently studied, so as the possibilities of their use for manure masses of different age.

Due to abovementioned, the search of universal reagent methods of decreasing the emission of odor-forming substances down to environmentally acceptable value is substantially important.

The purpose of this work is the search of possible solutions for the problem of decreasing the emission of odor-forming substances with simultaneous disinfection of hardly-processed pig manure slurries.

The task of the research is to identify universal chemical reagents, equally suppressing intensive microbiological decomposition of swine manure in lagoons under the open sky in anytime of the year and at different conditions of feeding of animals of different age, determination of optimal doses of the reagents decreasing the emission, comparison of the results of use of different reagents.

Experimental

Bedless pig manure with the humidity of 80-85% obtained from pig farm at village of Glebkovichy (Minsk region, Republic of Belarus) was used as a sample to perform necessary studies. The productivity of the farm is 100 pigs and the yield of pure manure is 1 m^3/day. The samples (10 liters each) were collected from swine farm lagoons during 6 months from January to December. In order to determine the influence of manure's age on the level of odor-forming substances and the quantity of reagents, required to control these emissions, the manure with different lagoon storage timewas investigated: fresh (stored in the lagoons for not more than 2 weeks), after 1-3-6 months after collection (manure was placed into clean buckets, closed with lids and stored at the conditions close to natural, until the time of analysis).

The presence of dry substance in the composition of liquid manure slurry was determined following the method [10]. The samples were placed in an oven and dried until constant weight at the temperature of 105°C; weighing was performed on laboratory scales «OHAUS» RV313 (AR3130), 2nd class of precision according to the standard GOST 24104-2001. The percentage of dry substance in the samples was varied from 15 to 25. Average contents of dry substance in liquid pig farm waste was 20%.

The measurement of pH was performed using professional multi-channel pH-meter «Seven Excellence» (METTLER TOLEDO, USA).

Several ways of

removing specific smell of the manure were investigated: changing the pH of manure slurry up to a certain level, when the emission of odor-forming substances is stopped: the method, based on oxidation-reduction properties of the reagents and the method based on inhibition of the development of bacteria by chemical reagents. In order to compare the degree of intensity of emission of volatile compounds three groups of reagents of different degree of action were selected and tested.

Due to the fact that substantial role amongst odor-forming substances is played by the ones possessing acidic and basic properties, sulfuric acid (H_2SO_4 conc.) and basic solution of sodium hypochlorite (NaClO 18%, марка А) were selected as reagents to treat the manure. There is an experience of using such group of reagents in animal husbandry: the level of pH is regulated in order to decrease the emission of odor-forming substances [11], meanwhile, sodium hypochlorite founds its use in veterinary due to the presence of fungicidal and bactericidal properties in it [12].

Peracetic acid $CH_3C(O)OOH$, ammonium persulphate ($(NH_4)_2S_2O_8$), formalin (CH_2O, conc. 37%) – each selectively taken component of this group of reagents is used for disinfection and/or deodorization of agricultural premices, in our work we investigated the possibility of their synergistic action to provide effective oxidation of odor-forming substances of manure slurry [13].

Sodium nitrite $NaNO_2$ and ammonium molybdate $(NH_4)_2MoO_4 \cdot 2H_2O$ were used as metabolic inhibitors, decreasing the activity of bacteria that is responsible for the production of odor-forming substances [9].

The components of disinfecting and de-odorizing compositions and their ratio were selected taking into account the minimization of toxic and dangerous effect on humans and animals.

The study of the influence of abovementioned additives on the emission of odor-forming substances was performed in the laboratory and semi-industrial conditions. At the laboratory conditions glass chemical beakers with the capacity of 1000 cm^3 were used to place the samples 0,5 kg each. Each group of reagents was introduced into the studied samples on its own scheme. One sample of manure slurry was used as a control one without any treatment. Different combinations of reagents and metabolic inhibitors were tested. After obtaining positive results, the influence of additives on decreasing unpleasant odor was performed in factory premises of the pig farm in 200 liter vessels, imitating lagoons with the manure.

The first set of studied reagents was acidified with the solution of 30% sulfuric acid until pH 5±0,5, afterwards to achieve total removal of unpleasant odor it was treated with alkali solution of sodium hypochlorite containing 3-5% of sodium hydroxide and 5-10% of sodium hypochlorite.

The treatment of 2nd set of the reagents was performed with the mixture of ammonium pershulphate (conc. 30%) and formaldehyde (conc. 30%) in the ratio from 1:3 to 3:1, exposure time – 24 hours, afterwards each of the samples was treated with the working solution of peracetic acid, in order to prepare this solution 4 parts of iced acetic acid, 1 part of hydrogen peroxide and 5 parts of water, acidified with boric acid with the additional of isopropanol (patent RU 2183467). It was experimentally established that freshly prepared solution of peracetic acid is less effective for deodorizing purposes, this is connected with the completeness of the reaction of turning acetic acid into peracetic, therefore, the solution was kept in a closed container for 3 days before the treatment was performed.

Third set of the samples of pig manure was treated with the mixture of sodium nitrite and ammonium molybdate in the ratio (20-40):(0,5-2) мМ.

The smell of pig manure is formed by complex mixture of the compounds with changing composition, therefore, the control of the intensity of the smell as a whole, not by the separate components, was performed.

The estimation of the odor was performed by organoleptic way. The group of 10 people, chosen randomly, was selected for testing. In order to determine, whether the testers can identify the difference between the smell of the tested sample and the smell of control sample, the method of pair comparison of total intensity of the smell according to the procedure described at GOST 53161-2008 (ISO 5495).

In order to estimate the smell, the samples of treated and dried manure, as well as non-treated manure (used as a control one) were presented to the testers. The samples in the quantity of 30 g each were placed into air-tight vessels, before performing the test they were kept in the dark during 24 hours at the temperature of (23 ± 2) °C. The quantity of the samples was adapted by the quantity of the testers in the group. The main requirement to the room for the tests was the absence of a foreign smell. The vessels used for the tests should have satisfied to the following requirements: they should not have any influence on test results and should be odorless.

After the stage of storage the smell of the atmosphere that has occurred in a limited space of the vessel with packing material or in packing material itself. The smell of such samples was tested immediately after opening the vessel. In order to perform the tests on the smell each tester sniffed the samples immediately after the lid was removed, upon completion of the test the vessel was closed again.

The samples were estimated on 5-point scale according to Table 1. If the difference between the estimates of the smell was greater than 1 point, the sample estimate was repeated not earlier than 30 minutes. The average of the results of estimates given by the testers was taken as a final result of the test. The results were rounded to a whole number.

Odor type	Grade	Point
Odor is not perceived	Excellent	0
Odor is perceived, it is not sufficiently expressed	Good	1
Moderate odor	Satisfactory	2
Strong odor	Bad	3
Very strong odor	Bad	4

Table 1. *Assessment of the intensity of manure odor*

Results and discussion.

It was established during the tests, that the intensity of the emission of odor-forming substances directly depends on the age of the manure. (Figure 1).

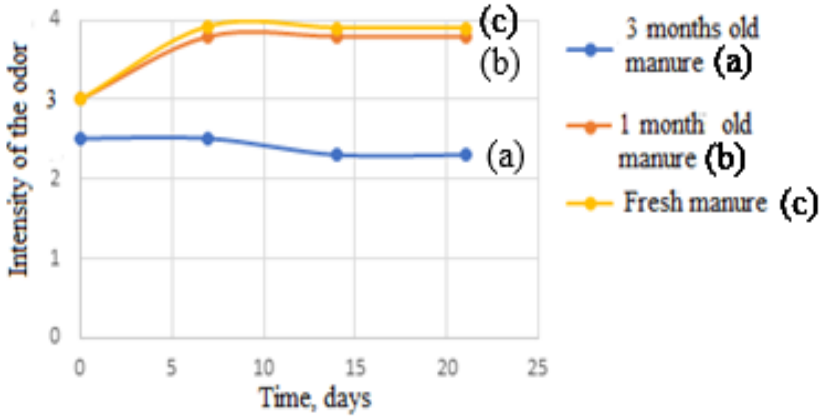

Fig. 1. *Dependence of the intensity of the smell on manure age*

In order to make an estimate of manure age on the intensity of the smell, non-treated fresh, 1 month old and 3-months old manure was studied. The intensity of the smell of fresh and 1 month old manure is the same during 21 days of study, it increases lightly starting from 6th day and then stays at the same level during the remaining time of the study. 3-months old manure has less expressed smell, that did not change during the entire study period, that allowed to decrease the quantity of reagents for the treatment of this manure mixture.

The results of research on deodoration of manure mixture with different reagents are presented at Figure 2 and Table 2. The decrease of the smell in samples treated by sulfuric acid and sodium hypochlorite is reasoned by bonding of volatile nitrogen-containing compounds into non-volatile ammonium salts and oxidation of hydrogen sulfide:

$$NH_3 + H_2SO_4 = NH_4HSO_4$$

$$H_2S + 4NaClO = 4NaCl + H_2SO_4$$

The formation of sulfuric acid as a result of treatment of manure by sodium hypochlorite allows to decrease the consumption of the first in order to achieve the positive results of the experiment. The effect of deodoration is achieved at the use of mentioned reagents due to the change of pH of treated samples and does not depend on the age of manure.

The results of treatment of manure depending on the pH of the media, presented on Figure 2, show that optimal pH value, when the emission of foul-smelling gases is stopped, equals to 5.

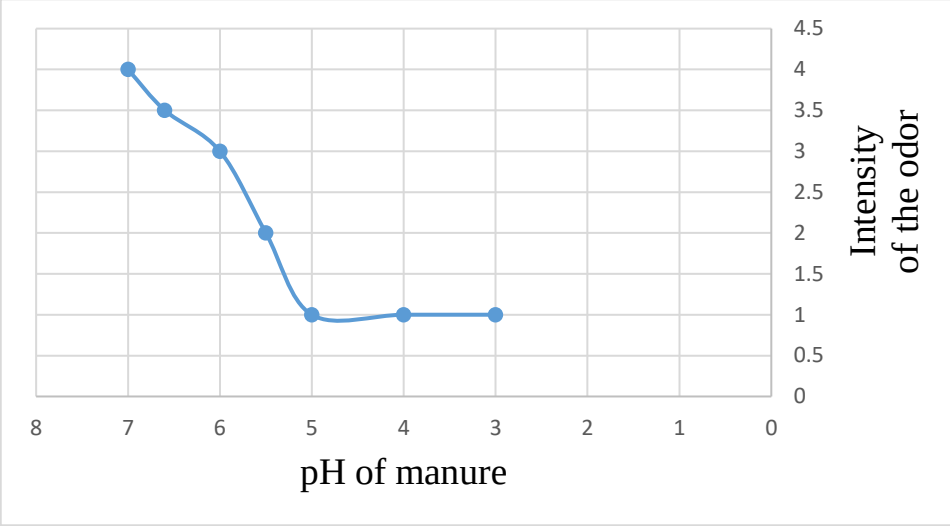

Fig. 2. *Dependence of the intensity of the smell of manure from pH of the mixture on the example of treatment with a mixture of sulfuric acid and sodium hypochlorite*

Stable normalization of the smell after the treatment with sulfuric acid and sodium hypochlorite was preserved during 6 days. It is necessary to note, that such time period is sufficient to provide subsequent total processing of manure into organo-mineral fertilizer.

The effect of deodoration at the use of ammonium persulfate as one of the components of de-odorizing mixture is mainly based on high oxidation ability of persulfate ion relation to sulfides of the manure and suppression of activity of anaerobic sulfide-forming bacteria. The authors of the work (US Patent 4160656 «Process for deodorizing liquid manure and removing harmful gases», MPKS 05 F 3/00, C 05 C 9/00 / H. Junkermann. Publ. 10.07.1979.) showed, that deodorizing effect of ammonium persulphate is enhanced in case, when formaldehyde is used in the mixture with persulphate. As in the work (US Patent 4160656 «Process for deodorizing liquid manure and removing harmful gases», MPKS 05 F 3/00, C 05 C 9/00 / H. Junkermann. Publ. 10.07.1979), at the treatment of manure with such mixture deodorizing effect was exhibited 15 minutes after adding the reagents and was preserved during 3 days, afterwards the unpleasant smell occurred again. Due to this the additional treatment of manure by the solution of peracetic acid was performed.

According to the data reported in literature [14], the mechanism of action of peracetic acid, that is a peroxy compound, is in destruction of bacteria – hydrogen-sulphide (-SH) and di-sulphide (S-S) bridges in proteins and enzymes. The deodorizing effect was preserved during 21 days after the treatment of peracetic acid (Figure 3).

High deodorizing effect of the reagents is explained by synergistic effect of the individual components of reagent mixture and also does not depend on the age of manure (so as in the case of treatment of sulfuric acid and sodium hypochlorite.

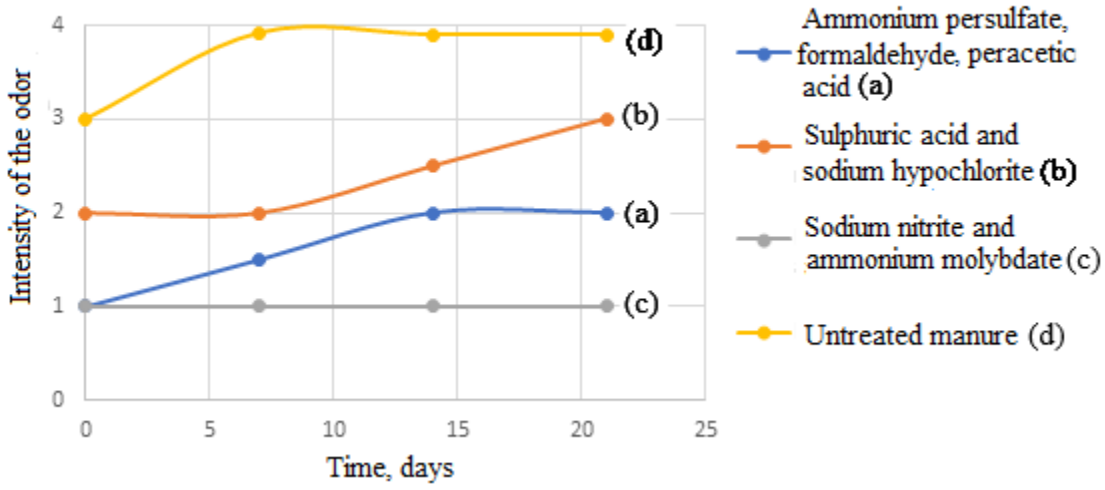

Fig. 3. *Dependence of the intensity of the odor of manure, treated with deodorizing formulations, on the time of storage after processing*

As a result of performed research on the treatment of manure mixture of different age with sodium nitrite and ammonium molybdate, it was established, that if only nitrite is added to manure mixture, the intensity of bad smell decreased only during 1 hour, the effect was preserved during

1 day. At the end of this time period the odor is stabilized and enhanced. Simultaneous or sequential addition of nitrite and molybdate substantially decreases the emission of odor-forming substances during the entire period of study (Table 2).

The addition of nitrite and molybdate to manure mixture promotes the oxidation of sulphides what leads to sharp decrease of the concentration of hydrogen sulphide in the manure during the short period of time and thus the removal of the unpleasant odor. The inhibiting effect of the mixture of sodium nitrite and ammonium molybdate is exhibited also in a decrease of the activity of sulfate-reducing bacteria and slowdown of the process of biogenic formation of sulphides.

Sodium nitrite concentration, мМ	Ammonium molybdate concentration, мМ	Days	Result, points
20	0,5	1	3
		5	3
		6-21	0
	1	1	3
		5	3
		6-21	0
	2	1	3
		5	0
		6-21	0
40	0,5	1	3
		5	0
		6-21	0
	1	1	3
		5	0
		6-21	0
	2	1	3
		5	0
		6-21	0

Table 2. *Assessment of the intensity of manure odor depending on amount of sodium nitrite and ammonium molybdate*

The volume of emitted odor-forming substances from pig manure and the quantity of reagents (sodium nitrite and ammonium molybdate) needed for the treatment of pig manure, depends on the age of manure: the increase of the age of manure (the term of its storage) leads to the gradual decrease of the content of odor-forming substances and, respectively, to the decrease of the consumption of chemical reagents required for the total removal of the odor.

Conclusion

The studies on selection of the compositions of chemical reagents providing disinfection and simultaneous deodoration of the manure from pig breeding complex were performed. It was established, that all three studied compositions of reagents (sulfuric acid in combination with sodium hypochlorite, ammonium persulfate combined with formalin with subsequent addition of peracetic acid and also the mixture of sodium nitrite and ammonium molybdate) provide disinfection and suppression of a bad smell of the manure, but more favorable from the point of view of suppressing the odor on a long term are the last two compositions (high de-odorizing effect was preserved during 21 days after treatment).

The manure mixtures, obtained as a result of such treatment, can be used as a main component at the production of the complex-organo-mineral fertilizers for their subsequent introduction into the fields under the different industrial crops.

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