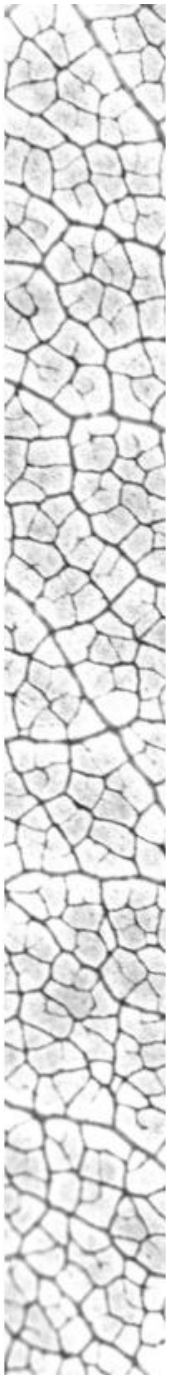

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Ammophos efficiency application for treatment highly concentrated by biogenic elements wastes of agro-industrial complexes

T. A. Kolesnikova [1*], M. A. Kulikova [2], E. A. Gribut [1]

[1] Senior Lecturer, Platov South-Russian State Polytechnic University (NPI). Novocherkassk, RUSSIA
[2] Associate professor, Candidate of Technical Sciences, Platov South-Russian State Polytechnic University (NPI). Novocherkassk, RUSSIA
*Corresponding author: tanechka-ko1986@yandex.ru

Abstract
Research findings are made of reagent treatment processes of highly concentrated liquid wastes at pig farms in agro-industrial clusters (AIC) for the purpose of obtaining organo-mineral fertilizer and water for irrigation and increasing the fertility of agricultural lands. The research objective was to study the process of reagent fractionation of highly concentrated by nutrient elements liquid wastes of pig farms, with the replacement of the existing superphosphate reagent by more effective nitrogen and phosphorus. The main processes of liquid waste separation into fractions, determination of optimal reagent doses, comparison of results of different reagents use and recommendations are studied. Optimal portioning of ammophos suspension for treatment of highly concentrated waste was established and determined by the effect of separation into fractions. Researches were carried out at Platov South-Russian State Polytechnic University (NPI) in Novocherkassk. The usage of ammophos for fractionation of highly concentrated liquid waste of livestock farms, is to use as an acidifying reagent ammophos suspension, reducing the retention time in wet pits, as well as reducing reagent doses by more than 2 times, compared with superphosphate. The efficiency of waste separation was provided with the usage of ammophos and superphosphate was compared, optimal doses of ammophos suspension -0.5-1.5 g/dm^3. The dependence of the separation efficiency of liquid waste as a function of its temperature was studied, the kinetics of separation at increasing temperature increases in the range from 20-45 ^{0}C. The greatest effect of separation of liquid waste was observed at a temperature of 45^{0}C, but the separation efficiency, ranging from 20 to 45 ^{0}C varies slightly. Nevertheless, it was accepted that the optimal temperature for reagent processing of highly concentrated liquid waste from pig farms of agro-industrial clusters was 20-25 ^{0}C.

Keywords: ammophos, agro-industrial clusters, organo-mineral fertilizers, high concentration liquid waste, fractionation

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INTRODUCTION

The import substitution process launched after the imposition of sanctions against Russia has led to a sharp development of agriculture, in particular, farms and business activities. At the same time, due to the high rate of natural resources exploitation in agriculture, there is, in particular, a rapid “expendability” of soil (Lassaletta et al.2019). Organic and mineral fertilizers are expensive in Russia, while in agriculture there are multi-tonnage wastes with high concentration of nutrients, containing these valuable components. When solving the problem of utilization of concentrated liquid wastes it is necessary to be guided by the strategy of sustainable development, the main element is the problem of natural resources and rational nature management effective usage (Russian Federation Government Order of 02.02 of 2015 № 151-R 2017). The relevance of the usage of liquid waste from pig farms is due to its properties and peculiarities. Concentrated liquid waste is a universal organic fertilizer (Bondarenko and Kachanova 2016, Bondarenko et al. 2010) in the form of a suspension, the disperse medium of which is an aqueous solution of mineral salts, organic compounds, as well as colloidal solutions, and the disperse phase - solid particles of excreta, fodder and some mineral inclusions. Dry substance contained in colloidal solutions can be isolated only when special treatment methods are used

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(Fournel et al. 2019, Riano and Garsia-Gonzalez 2014, Strogiy 2014, Wang et al. 2016).

Highly concentrated wastes of agro-industrial clusters, first of all, liquid wastes of pig farms at reagent treatment become suitable for irrigation of agricultural lands, as they contain valuable components in the form of N,P,K (De Oliveira et al. 2011, Dhyani et al. 2018, Garzanov and Dorofeeva 2018, Zhou et al. 2019).

Liquid fraction of liquid waste has a high fertilizer value and meets the requirements of surface irrigation by means of sprinkling. The formed sediment belongs to organo-mineral fertilizer, which application can be especially effective on acid soils (Zhang et al. 2019). A narrow range of reagents for destabilizing the colloidal system of concentrated liquid waste should be considered as an unsolved problem in this area. Chemical reagents used for treatment of concentrated liquid waste are in some cases introduced into the soil. Reagent fractionation with the use of mineral fertilizers is a non-destructive method to preserve and increase nutrient elements. In this case, water is used twice - first for self-alloy of manure, and after reagent separation - for crop irrigation (El-hamady 2017).

The cluster approach is considered appropriate for creating a model for planning a business strategy for waste management (Brockmann et al. 2014, Makara and Kowalski 2018, Putri et al. 2015, Swaney et al. 2018, Willems et al. 2016, Winkler et al. 2016). The article (Fernandez-Mena et al. 2016) outlines the basic principles of agro-industrial cluster formation and nutrient flow management in agri-food systems.

The interest of scientists (Egea et al. 2018) is to create an integrated and sustainable model of biobased economics of agro-industrial clusters. Competitive clusters should include the following elements: livestock complexes, agricultural land for fodder crops, workshops for the production of feed and organo-mineral fertilizers from waste, research institutes of agricultural and polytechnic universities.

In modelled agro-industrial clusters, there should be maximum usage in development section, consistent with the principles of best available technology.

In continuation of works on the use of liquid wastes concentrated on nutrients of industrial clusters it is necessary to develop non-destructive resource-saving technologies of their utilization using reagents. Such technology requires a detailed study of resource-saving and environmental safety issues in the utilization of concentrated liquid waste. In this case, it is necessary to study the impact of the used reagent on ecosystems at various levels, including artificial ecosystems (agro-ecosystems), which can result in deodorizing effect, reducing the emission of stink gases into the atmosphere and, consequently, reducing the size of the sanitary protection zone. The introduction of this technology in the utilization of concentrated liquid waste of high agronomical amelioration value helps to reduce environmental damage while reducing the production of minerals for fertilizer production with equivalent nutrient inputs (N, P, K).

It is necessary to scientifically substantiate the environmental principles of technological solutions that ensure environmental safety during processing and efficient utilization of concentrated liquid waste from agro-industrial clusters.

RESEARCH OBJECTIVE

A large number of experimental studies are devoted to studying the mechanism of liquid waste separation. However, there are no data in the literature on the application of ammophos as a reagent for the treatment of liquid wastes of agro-industrial clusters.

The research objective was to study the process of reagent treatment of liquid wastes from pig farms with the replacement of neutralizing reagent superphosphate with a complex previously unexplored mineral reagent.

The main concept of the authors, when processing liquid waste from pig farms, is the use of mineral fertilizers as a reagent, which are used in agricultural production. Mineral fertilizers are firstly used as reagent for acidification after treatment with $Ca(OH)_2$ or sludge CaC_2, and then they are applied to agricultural fields as organo-mineral fertilizer. The concept is poorly studied and there are few publications in modern scientific literature.

Among the tasks were: studying the main processes of division into fractions of complex colloidal system of liquid wastes of pig farms; determination of optimal doses of reagents, comparison of results of using different reagents.

CONDITIONS, MATERIALS AND METHODS

There is a technology that includes the use of $Ca(OH)_2$ or sludge CaC_2 with subsequent introduction of simple superphosphate (28% active P_2O_5) with a concentration of 3.0-6.0 g/dm^3 (Kolesnikova et al. Surzhko and Kulikova 2011). The authors studied the possibility of replacing superphosphate with ammophos (52% active P_2O_5 and 10-12% active N).

The research was carried out in Platov South-Russian State Polytechnic University (NPI). The research object was a liquid waste of pig farm in “Batayskoye” (Rostov region) with productivity of 30 thousand pigs, with consumption of liquid waste 150 m^3/day. Researches on definition of optimum parameters of process of division of liquid wastes of pig farms of agro-industrial clusters into fractions were conducted in standard cylinders of 1dm^3. Before the test the liquid waste was defended for 1 hour, then it was filtered through sieves with hole sizes 3-5 mm. To determine the temperature and pH of the liquid waste we used the ionizer I-160MI with the electrode ES-10603/7 K80.7. Electrodes for measuring hydrogen ions were

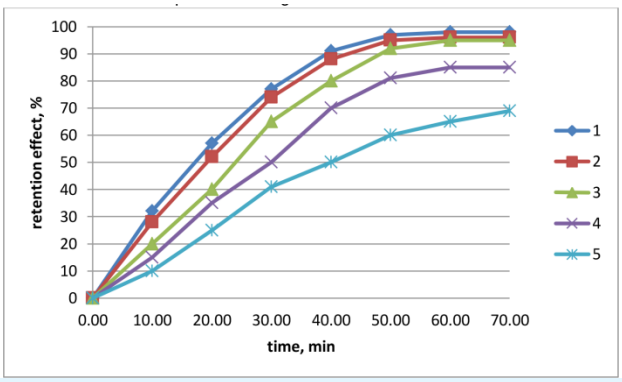

Fig. 1. Dependence of separation efficiency on dose of introduced ammophos.1-1,82 mg/dm^3, 2-1,3mg/dm^3, 3-0,78mg/dm^3, 4-0,65 mg/dm^3, 5-0,4mg/dm^3.

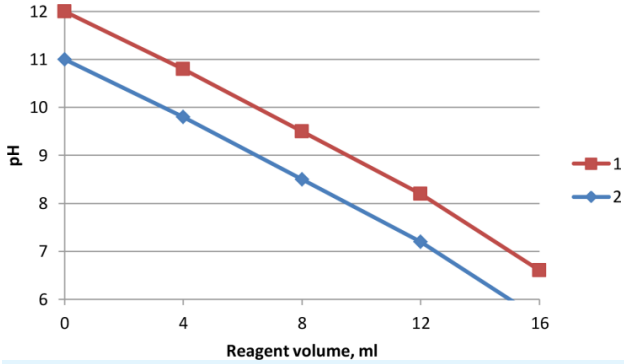

Fig. 2. Dynamics of liquid waste pH reduction depending on the initial pH: 1-12; 2-11

prepared according to the instructions of the ionizers. Liquid wastes of agro-industrial complex were studied to determine their dry matter content (Lourie and Rybnikova 1974). A drying cabinet with a heating temperature of 105^{0}C was used; laboratory scales of 4 accuracy classes were used. As a result, it was found that the percentage of dry matter in different layers of the total volume of fresh waste varied from 1 to 7. The average dry matter content in the liquid waste of the pig farm after intensive mixing was 3%.

Optimal dose of ammophos suspension for treatment of highly concentrated liquid wastes of agro-industrial complex was determined by the effect of separation into fractions. For this purpose in 5 identical samples were introduced at the first stage of CaC_2 2g/dm^3 on active CaO. The pH value in each sample was determined, after intensive mixing at such a dose of CaC_2 the pH value was increased to 12. At the next stage acidifying reagent-suspension of ammophos was introduced. For this purpose different doses of 30% of ammophos suspension were introduced into the test samples: 0.4; 0.65; 0.78; 1.3 and 1.82 g/dm^3 (according to active P_2O_5) at stirring for 2-3 minutes, thus reducing pH to 6.5-8.5. After gravitational settling the mixture was divided into transparent liquid fraction and sludge – organo-mineral fertilizer.

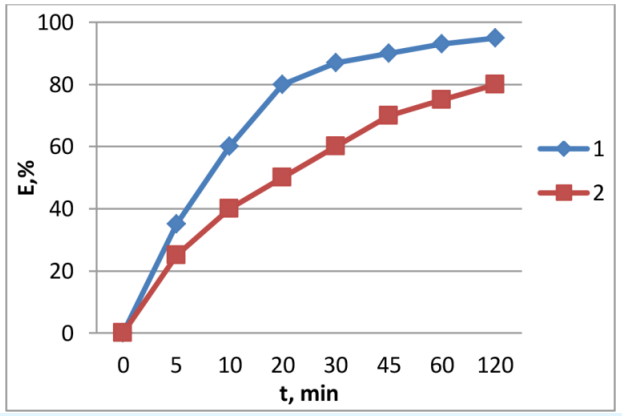

Fig. 3. Dependence of the retention effect on time at different cylinder diameters, mm: 1- 100; 2-45

RESULTS AND DISCUSSIONS

Research results are depicted in **Fig. 1**.

The results of studies have shown that the optimal dose of introduced ammophos was 0.5-1.5 g/dm^3. Such doses are several times lower than the doses of previously used superphosphate (3.0-6.0 g/dm^3).

The dynamics of pH reduction of liquid waste after the introduction of ammophos suspension is shown in **Fig. 2**. Liquid waste sediment formed after separation was large flakes of grey color, capable of compaction.

Researches have shown that the required quantities of ammophos suspension required to bring the pH value of the mixture to 6.5-7.5 depend on the initial pH (before acidification) and, accordingly, the initial dose of the suspension of lime milk. To reduce the pH value from 11 to 7.5 per 1 dm^3 of waste, 10 cm^3 of ammophos suspension was required, from 11 to 6.5 - 12 cm^3 of reagent. At treatment of liquid wastes of pig complex, having up to acidification pH=12, ammophos suspension was required already 12 and 16 cm^3 per 1 dm^3.

Dependencies of sedimentation effect on time at different cylinder diameters are established, which are shown in **Fig. 3**. The kinetics of sludge thickening is as follows: after 10 minutes sludge volume was 59% of the total mixture, after 30 minutes - 82%, after 45 minutes - 95%. The most thickened sludge, which is an organo-mineral fertilizer, is generated after 45 minutes, which allows the design of a liquid waste storage facility for this time rather than for 2 hours, which is used in practice. This will significantly reduce the volume of structures and the capital costs of their construction.

It is necessary to notice that processing by reagents has allowed receiving considerable deodorizing effect that in the future will allow reducing the sizes of a sanitary-protective zone.

The final effect of separation of liquid waste into fractions in the cylinder of 100 mm was 95%, and in the cylinder, with a diameter of 45 mm - 80%.

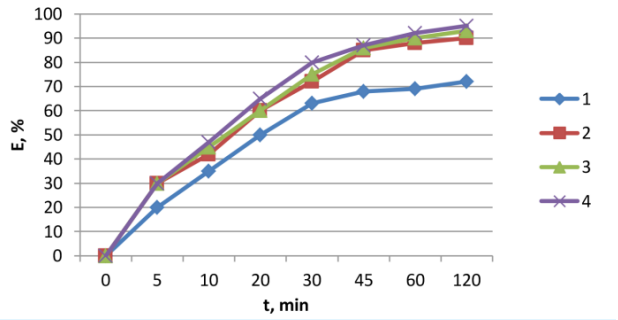

Fig. 4. Dependence of the effect of division into liquid and solid fractions at ammophos dose of 0.5-1.5 g/dm^3 on temperature, ^{0}C: 1-10; 2-20; 3-30; 4-45

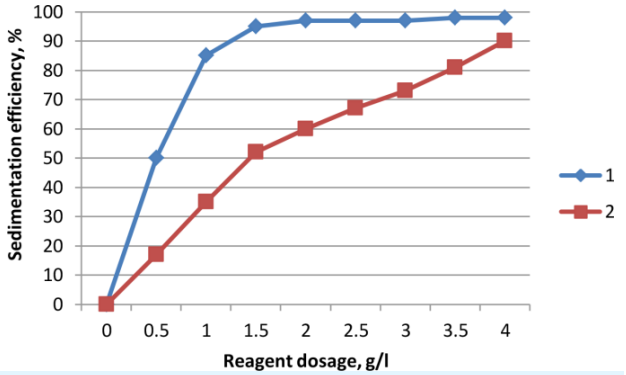

Fig. 5. Dose dependence of waste separation effect on liquid and solid fractions, when using 1-ammophos; 2-superphosphate, mg/dm^3

It is established that the effect of separation of liquid waste into fractions is achieved after 45 minutes and is 92% in a cylinder of 100 mm diameter and 75% in a cylinder of 45 mm diameter. So, during designing it is necessary to take into account the geometric dimensions of wet pits.

In order to study the influence of temperature conditions on the process of reactive separation of liquid waste into fractions, they were treated at different ambient air temperatures. The dependence of the effect of separation of liquid and solid fractions from time at different ambient temperatures is shown in **Fig. 4**.

Studies have shown that the separation rate increases as the temperature rises. In the range from 20-45 ^{0}C the greatest effect of separation of liquid wastes of agro-industrial complex was observed at the temperature of 45^{0}C, however, the separation efficiency, starting from 20 to 45 ^{0}C is approximately the same. Therefore, an optimal temperature for reagent treatment of highly concentrated liquid waste can be considered 20-25 ^{0}C.

The dependence of the separation effect on dose was compared with the use of two different acidifying reagents - ammophos and previously studied superphosphate. The results are presented in **Fig. 5**.

The comparison results of two acidifying reagents showed that the effect of separation into liquid and solid

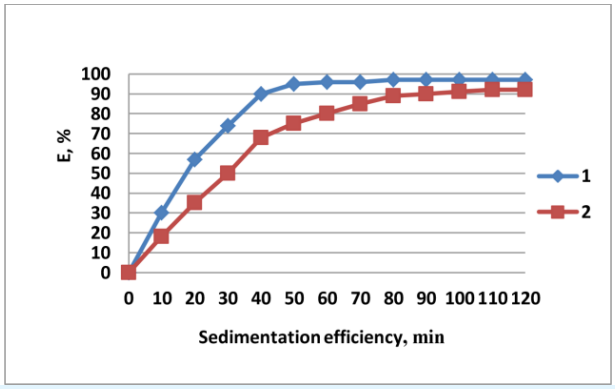

Fig. 6. Dependence of the efficiency of the reagent fractionation of waste water on the retention time of using 1-ammophosphate 2-superphosphate

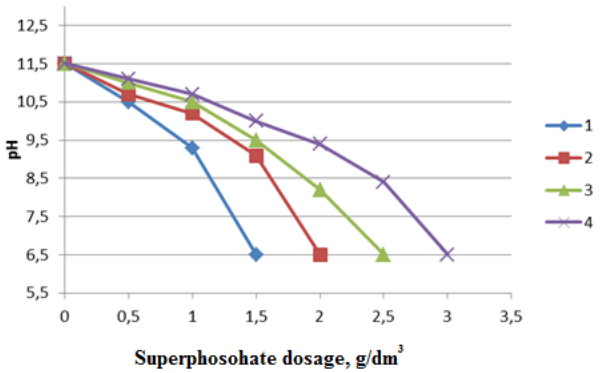

Fig. 7. Dependence of pH on ammophos dose at solid matter content: 1-1%; 2-3%; 3-5%; 4-7%

fractions when using superphosphate was 90%, and ammophos allowed increasing the efficiency of reagent fractionation of liquid waste up to 95%. At the same time, the retention time was reduced from 120 to 40 minutes.

Optimal doses of ammophos suspension at reagent fractionation of liquid wastes of agro-industrial clusters with different dry matter content of **Fig. 7** were determined.

Researches have established that doses of ammophos are directly proportional to the content of dry substance in liquid wastes of agro-industrial clusters. So, with increasing the solid content in the initial liquid waste from 1 to 7% to reduce pH from 12 to 6.5, the effective dose of ammophos increased from 0.5 to 3.0 mg/dm^3.

As a result of the research, optimal conditions for the efficient use of the ammophos suspension instead of the superphosphate suspension for the treatment of highly concentrated agricultural cluster wastes were established.

The researches allow developing the technology of treatment of highly concentrated liquid wastes of pig farms of agro-industrial complex with obtaining organo-mineral fertilizer and irrigation water.

The technology meets the criteria of the best available technologies, such as resource saving and waste-free production. All applied reagents are fully used in agro-industrial clusters.

The results of research on the use of ammophos as a reagent can be used in the design and reconstruction of facilities for treatment of liquid waste in agriculture.

Wastes from pig farms, stored in accumulators, can also be processed into organo-mineral fertilizers.

Processing of liquid wastes of pig farms with obtaining organo-mineral fertilizers and irrigation water can significantly reduce their negative impact on agro-landscapes and atmospheric air.

For the most detailed elaboration of the highly effective technology of liquid waste fractionation of agricultural clusters with the use of previously not applied acidifying reagent, it is necessary to conduct research on the properties of the resulting sludge, in particular: the determination of specific resistance (moisture content), sludge thickening at different modes of mixing, the ability to mechanically dewater. Further research on the reagent fractionation using ammophos also includes the desodorization process.

Consequently, the high efficiency of ammophos suspension application for treatment of agro-industrial clusters wastes highly concentrated by biogenic elements has been confirmed. Improvements of process technology of highly concentrated liquid wastes in agro-industrial clusters have been proposed. It allows to reduce time of sedimentation in wet pits, and also to reduce doses of coagulant more than in 2 times.

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