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The technology of water separation and purification after anaerobic digestion of liquid manure, and biofertilizer production from organic sludge

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In the wake of the man's household activity, large quantities of organic waste are created and their accumulation leads to serious ecological and social problems. Even though in most cases organic waste can be reused in the household and energetics sectors, due to the variety of different chemical components, the complex technology of the waste management and recycling is yet not available in the market. One of the most universal ways to utilize the household and agricultural waste is anaerobic fermentation, which not only degrades waste, but provides the benefit of the energy from emitted bio-gas. However, this method does not completely solve the task of total waste reprocessing into an economically profitable product. Also, after the emission of bio-gas, liquid organic waste still occupies a large volume, has a foul smell and might have toxic substances and pathogenic microorganisms. In this study, the organic household and agricultural waste management technologies, used in the last decades, are discussed and summarized, the sequence of water separation and purification processes and the ways to degrade organic compounds and liquidate undesirable scents are suggested. The results of completed research are presented. During technological processes, water was separated from liquid manure and purified. After the treatment of slurry of concentrated organic components, the dry, sterile and odourless complex of organic and mineral compounds, that can be used for soil fertilization, has been obtained.

Key words: slurry, manure, separation, deodoration, biofertilizers, waste, utilization

INTRODUCTION

As urbanization, industrialization and agriculture development increases worldwide, so does the amount of waste that are produced along with it. Thus, the main anthropogenic contaminants are derived from industry, energetics, transport and agriculture.

Agriculture is often divided into sectors and the highest amount of wastes derives from poultry and cattle farming. The biggest part of these wastes is composed of slurry and manure. Manure is one of the most important organic fertilizers. Depending on the amount of litter, manure can be liquid, half liquid or dense. However, manure, in its unaltered condition as a fertilizer, can lead to severe environmental problems [1].

When used as a fertilizer, livestock and poultry manure can provide valuable organic material and nutrients for crop and pasture growth. However, nutrients such as nitrogen and phosphorus can degrade water quality if they are overapplied to land and enter water resources through runoff or leaching [2]. Moreover, the livestock sector generates, on a worldwide basis, more greenhouse gas emissions than the transport sector. It is the most significant contributor to land and water degradation [3]. Manure has several components that can pollute water. These include oxygen-demanding materials (organic matter), plant nutrients, and infectious agents. Colour and odour is also an important matter to deal with.

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Manure composition and management

Manure composition primarily depends on the animal feed, their bedding and the species of livestock. However, the main components are the following: excreta, urine, bedding, water, feed leftovers. All those components have high amounts of organic matter, volatile odorous compounds and minerals in various states that are important for the use of manure as a fertilizer. Since most of those minerals (phosphorus, ammonia, potassium) are in an insoluble or volatile state, that is not readily available for the plants and lost if applied directly, manure composting is a common practice. However, nitrogen loss by gaseous emissions during the composting process causes not only a decline of compost value as a fertilizer, but also serious environmental risks such as odour problems, global warming and depletion of stratospheric ozone [4, 5]. Moreover, the organic materials in manure are abundant and their degradation requires time. The bacteria, naturally found in manure or sometimes artificially added to the compost to speed up the degradation, enhance this process. Nevertheless, amendments are needed to stop the leakage of organic matter especially in case of liquid swine manure. It is done by mixing manure with different organic wastes used as bulking agents (biochar, coffee husk, sawdust) to create humic-like substances that are more approachable for degrading bacteria [6].

A wide range of technologies is available for waste handling and processing. The most common is composting which is used for organic waste and produces valuable organic fertilizers. Yet, there is some recent information concerning health risks derived from occupational exposure to organic dusts, bioaerosols and microorganisms in composting plants [7]. The second, similar to composting, is anaerobic digestion (AD) that produces valuable biogases, i. e. methane. AD doesn't remove the nutrients from manure; in fact, the organic nitrogen is converted to ammonium, which is more available to plants. However, digestion produces solid fibres and polluted liquids that have to be decontaminated and disposed of.

Here, we discuss the techniques for manure processing that are being widely used nowadays. Mechanical separation methods, based on sieves, belt and screw presses, generally achieve a ~20% reduction of the liquid volume. These separators generally partition P or N in proportion to liquid and fibre fractions. The decanting centrifuge, geo-textile tubes and settling basins achieve good solid and nutrient separation. Settling basins may be less appropriate because there could be more odours. These technologies have the potential to partition a higher proportion of P and (to a lesser extent) N in the separated solid fraction than in the liquid fraction.

The use of chemical additives, particularly polymer flocculants, is a well-established industrial technique for precipitating solids and minerals in waste streams. When used with polymer flocculants and associated additives, decanting centrifuges and geo-textile tubes can achieve very high levels of partitioning of P and total N. Polymers could possibly be used with other mechanical separators, but little work seems to have been conducted on this [8].

Mechanical decantation technologies require time and / or energy and don't assure the separation of all soluble organic components such as phosphates or the microorganisms that reside in water. Chemical technologies, such as flocculants, are used to aggregate the organic particles. The most widely used are aluminium and ferrum salts. However, those chemicals release metal ions into the environment, thus a more environmentally friendly technology is required. Therefore, coagulation can be done using calcium chloride, which is not toxic to the environment and has a positive impact on soil.

Decontamination and stabilization

When dealing with manure and other waste disposal, problems arise due to the possible infections, caused by microorganisms present in the waste e. g. *Clostridium* spp., *Salmonella* spp., *Yersinia* sp., *Campylobacter jejuni, Listeria monocytogenes, Escherichia coli* and so on. Recent studies show that even the anaerobic digestion can not sufficiently remove the pathogenic bacteria, especially the spore forming ones [9, 10]. Furthermore, the mesophilic biogas production (38 °C), due to the process' temperature is more unreliable than the thermophilic one (55 °C) in destroying the pathogenic bacteria [11]. Therefore, an additional treatment of waste is needed for the decontamination of water and solid materials produced after the biogas extraction.

Another problem that is very prominent in biological waste management is the odours that are being produced during manure biodegradation. The malodours mostly come from volatile compounds such as alcohols, carbonyl compounds, terpenes, esters, sulphuric compounds, ethers, ammonia and volatile amines, indoles and phenols [12, 13].

After the anaerobic digestion of organic waste and the separation of organic components from sludge, as it was mentioned before, the leftover material is potentially hazardous to the environment. However, some biogas extraction technology researchers have different opinions about the contaminant hazards and suggest using the partly digested sludge directly onto soil without any other treatment [14]. Nevertheless, taking into account all the facts it is clear, that even with excellent properties, sludge is a likely place for pathogenic microbe growth when it is being transported or stored. Moreover, the malodours of the sludge is a huge problem, too. So are the concentrated amounts of nitrogen and organics that can leach to surrounding areas. Organic waste stabilization is usually done by means of biological and chemical processes. The possible ways of stabilization are: aerobic (aerobic tank), anaerobic (composting in a gas reactor), composting, stabilization with limestone, stabilization using chemical amendments, pasteurization in >70 °C temperature, drying in >100 °C temperature, burning [15]. However, those methods do not fully remove the malodours, nor deal with the problem of leaching and contamination.

A perspective way of sludge treatment is chemical – using aggressive reagents such as mineral acids. Despite the simplicity of the technology and the problems of acid usage, it is a quick and efficient way of waste decontamination and odour removal. The neutralization of reactive reagents is a fairly simple process since the technologies for that are being used all over industry (e. g. leather production).

Taking into account the existing problems of waste degradation and the solutions that are being suggested, we have developed a strategy for a complex manure management system. Using the research results we have outlined a specific technology for the treatment of manure after biogas production. It involves the separation and purification of water from the organic components and decontamination of the leftover sludge, making it into a sterile, odourless organic and mineral fertilizer that can be safely transported, stored and used in agriculture.

MATERIALS AND METHODS

Materials

The research was conducted using swine slurry derived after anaerobic digestion in JSC "Biocentras" laboratory. Dolomite bought from JSC "DOLOMITAS" (Lithuania). All processes and reactions were performed using reagent grade materials.

Methods

Total microorganism count

The determination of total microorganism growth was performed using spread plate method. The samples were suspended in 0.9% sodium chloride solution and then spread onto a nutrient agar medium ("Oxoid") plates. The plates were kept at 30 °C for 48 hours and afterwards the CFU's (colony forming units) were counted.

Organic component and water separation

During the experiments, 12 ml of anaerobically digested slurry was poured into 15 ml flasks with lids. Different amounts of 4 M $CaCl_2$ solution were added and the flasks were centrifuged at 4 500 rpm. The intensity of organic component sedimentation was measured. Separation effect was evaluated comparing the centrifuged dry component amount with the total slurry sample dry component amount:

$$\eta = \frac{m}{M} \times 100\%$$

η – efficiency coefficient, %;
M – slurry dry material amount, g;
m – sedimented sludge dry material amount, g.

Separated water purification

400 ml of slurry was mixed with 4% (according to volume) of 4 M $CaCl_2$ solution and centrifuged at 4 500 rpm for 3 minutes; the supernatant was separated afterwards. To ensure the thorough mixing (shaker IKA LH, speed – 250 rpm) an equimolar amount of ammonia phosphate was added to the amount of used $CaCl_2$. After the sedimentation of calcium phosphate the mixing was stopped and the liquid separated and filtrated through a paper filter.

Sedimented sludge decontamination

Sedimented sludge (moisture – 72%) was mixed with concentrated sulphuric acid and hydrogen peroxide (30%) solution. Sulphuric acid was selected as a strong oxidizer and hydrolysis catalyst, which can not only destroy the microorganisms but also break down the organic structures, while hydrogen peroxide acts as an oxidizer and regenerates sulphuric acid. After 15 minutes of reaction, without stopping the stirring, the reaction mix was neutralized using equimolar amount of dolomite $CaMg(CO_3)_2$. The calcium phosphate gel acquired during organic component sedimentation was also added to the mix. The smell and structure of the complex was evaluated during all parts of the experiment.

RESULTS AND DISCUSSION

Soluble and insoluble material sedimentation from slurry using $CaCl_2$ has shown that this process is quite effective. Using rather small amounts of $CaCl_2$ and centrifugation, almost 99% of anaerobically digested slurry organics can be separated from water (Fig. 1). Total solids sedimentation was less than 50% when slurry centrifugation was performed without any added chemicals (Fig. 2). Using 4 500 rpm speed and 1–2% of 4 M $CaCl_2$ solution, after 2–3 minutes of centrifugation the maximum affect of water separation from slurry is achieved. Thus, using this technology in a decanter, water separation from sludge should be fast and 1 000 litres of slurry would only require 4.44 to 8.88 kg of solid calcium chloride.

The separated water, which is full of calcium and chloride ions, mixed with ammonia phosphate solution produces a calcium phosphate gel that absorbs the free ions and positively charged organic components left after the decantation. Calcium phosphate gel sediments onto the flask in, approximately, 10 minutes. Organic component sedimentation and calcium phosphate gel formation are shown in Fig. 3.

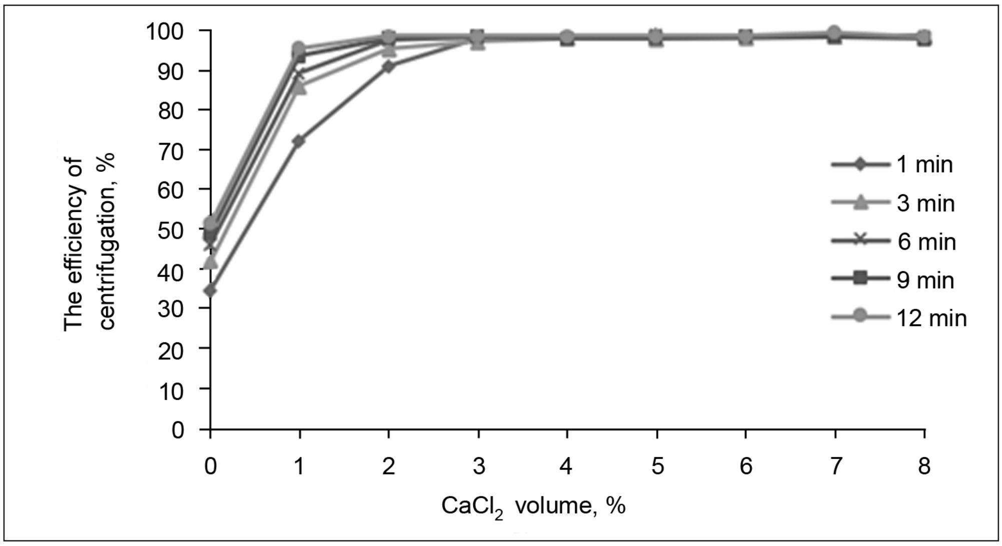

Fig. 1. Centrifugation efficiency, depending on the amount of $CaCl_2$

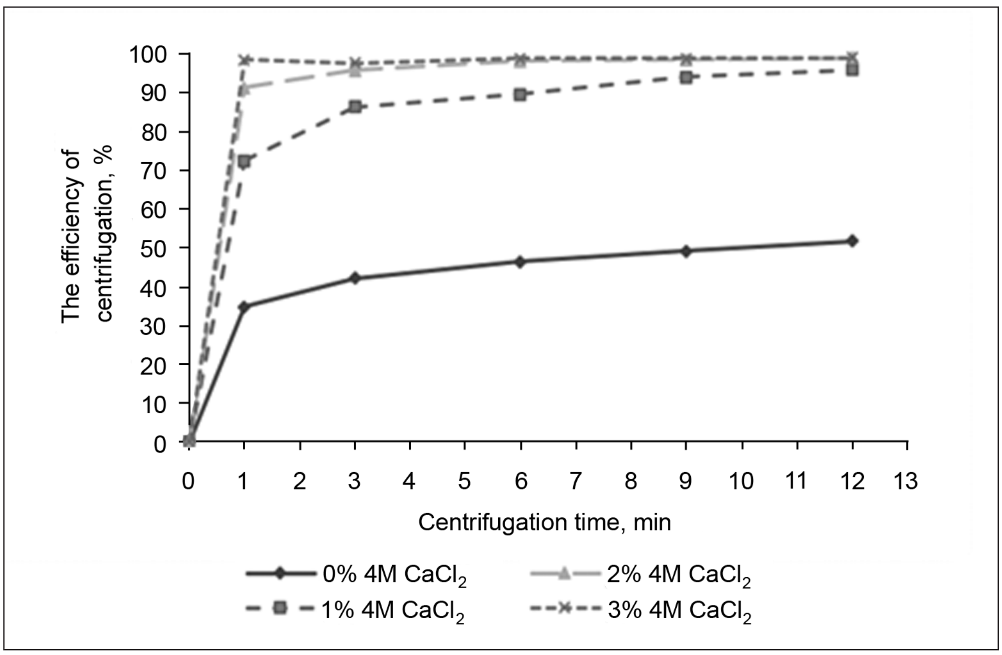

Fig. 2. Centrifugation time correlation with dry material from slurry sedimentation efficiency

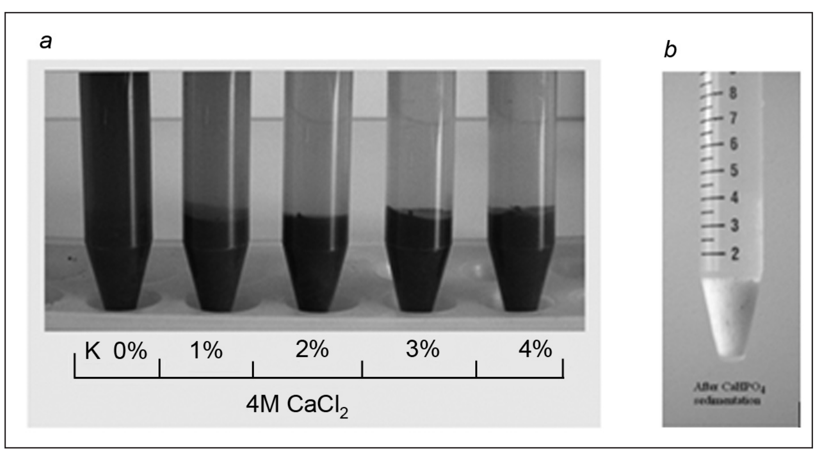

Fig. 3. Water separation and purification from slurry compounds: *a* – sedimentation after centrifugation (4 500 rpm, 3 min) with different amounts of calcium chloride (K – control sample without $CaCl_2$); *b* – separated with 2% of 4 M $CaCl_2$ slurry liquid after $CaHPO_4$ forming and sedimentation

Filtering the water from leftover calcium phosphate particles produces such organoleptic qualities as colour, smell and clearness that are the same as in tap water. After the microbiological water testing, no microorganisms were found in the samples. The ammonia and chloride ions that may reside in water after the processes can be eliminated using ion exchange reactions that are proposed in some papers [16, 17].

Furthermore, after the sedimentation sludge was mixed with concentrated sulphuric acid and hydrogen peroxide (30%) solution (as described in the methods) ensuring the thorough mixing, thus, organic material oxidation and hydrolysis took place. Due to the violent reaction type the reaction mixture was heated and a small amount of smoke has been produced. After the gas stopped evaporating the separated calcium phosphate gel and dolomite powder was added to the mixture and a neutrally smelling, dark grey colour organic and mineral complex was created. The dried complex contains organic compounds that are merged into the inorganic calcium and magnesium sulphate and phosphate matrix. 1 g of the mixture was homogenized and suspended in 9 ml of 0.9% sodium chloride solution and spread onto solid nutrient ("Oxoid") medium. After 48 hours of incubation at 30 °C temperature microbiological growth was not seen. Smell neutralization and microorganism decontamination required only 3% of concentrated sulphuric acid and 2% of H_2O_2 in respect to the total reaction mixture volume.

Optimal conditions for the processes, chemical complex analysis and other important questions for this topic will be analyzed during the following research. Nonetheless, the results of these experiments are concluded in Fig. 4.

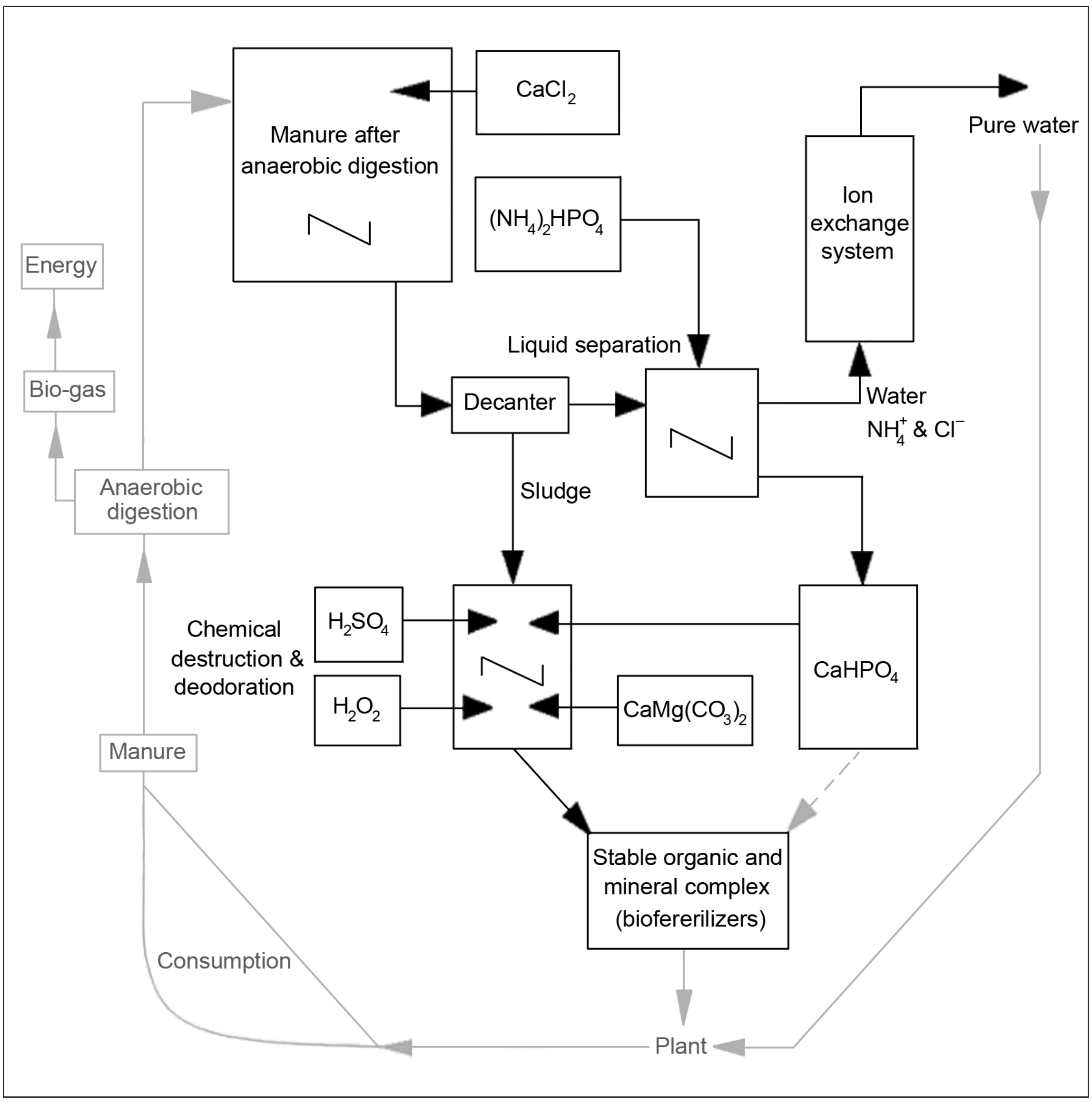

Fig. 4. Basic technological scheme for the separation, decontamination and production of stable odourless fertilizer from anaerobically digested swine slurry

CONCLUSION

To conclude the results of the research, after analyzing the topic related literature we can say that one of the most complex organic agricultural waste degradation methods is anaerobic digestion together with the following water separation and sludge stabilization stages.

During the research, a technology for water separation and purification from anaerobically digested swine slurry was developed and a method for sludge concentration, decontamination and modification into a fertilizer was proposed. The technological advantages of this method are outlined hereafter: the processes of this technology are fast and can be carried out continuously; operations are industrially applicable, standard and uncomplicated. Calcium chloride used for water separation is ecologically friendly compared to the usually applied coagulants made of ferrum and aluminium salts. The technology is fast in smell reduction and microorganism decontamination. Most of the reagents used during the processes are a part of the end product, and their amounts are relatively small. Reagents such as sulphuric acid are commonly used in the mineral fertilizer industry; our proposed technology not only produces calcium-magnesium sulphates, but also decontaminates organic components, destroys malodours and immobilizes organic complexes. The fertilizer produced using this technology has many advantages because the organic components are immobilized in the mineral matrix, which should prevent fast leaching and ensure its prolonged activity. Furthermore, mineral components should, in their turn, stabilize soil pH during the process of nitrification, when soil pH levels drop and the inorganic matrix begins to melt releasing minerals and organic components into the environment. This technology can be applicable not only to the agricultural anaerobically digested waste, but also to other biodegradable pollutants such as household waste and sewage.

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VANDENS ATSKYRIMO IŠ ANAEROBIŠKAI APDOROTŲ SRUTŲ, IŠVALYMO BEI ORGANINIO DUMBLO PERDIRBIMO Į BIOTRĄŠAS TECHNOLOGIJA

Santrauka

Dėl žmogaus ūkinės veiklos susidaro dideli kiekiai organinių atliekų, kurių kaupimasis sukelia rimtas ekologines ir socialines problemas. Nors daugeliu atveju organinės atliekos gali būti pakartotinai naudojamos žemės ūkio ir energetikos sektoriuose, dėl atliekų skirtingų cheminių komponentų įvairovės kompleksinės atliekų tvarkymo ir perdirbimo technologijos dar nėra. Vienas universaliausių žemės ūkio ir buitinių organinių atliekų panaudojimo būdų yra anaerobinė fermentacija: jos metu vykstančios atliekos išskiria biodujas, kurias galima panaudoti. Tačiau šiuo metodu iki galo neišsprendžiamas visiškas atliekų perdirbimas į ekonomiškai rentabilų produktą, nes po biodujų išsiskyrimo skystos organinės atliekos tebeužima didelį tūrį, yra nemalonaus kvapo, jose gali būti toksinių medžiagų bei patogeninių mikroorganizmų.

Šiame darbe trumpai aptariamos ir apibendrinamos pastaraisiais dešimtmečiais naudojamos organinių žemės ūkio ir buitinių atliekų tvarkymo technologijos, pasiūloma vandens atskyrimo ir išvalymo procesų seka, organinių komponentų destrukcijos bei nepageidautinų kvapų likvidavimo būdas. Pateikiami atliktų tyrimų rezultatai. Technologinių procesų metu iš skysto mėšlo buvo atskirtas ir išvalytas vanduo, apdorojus sukoncentruotų organinių komponentų dumblą gautas neutralaus kvapo, sausas, sterilus organinių ir mineralinių medžiagų kompleksas, kuris galėtų būti naudojamas dirvožemio derlingumui pagerinti.

Raktažodžiai: srutos, mėšlas, atskyrimas, kvapų panaikinimas, biotrąšos, atliekos, utilizacija