Article

Influence of Gypsum-Containing Waste on Ammonia Binding in Animal Waste Composting

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Abstract: The possibility of using gypsum-containing waste–citrogypsum, which is a by-product of the chemical biosynthesis of citric acid, was considered as an additive for composting poultry manure from poultry farms that practice litter-free poultry keeping. The research was carried out on an experimental batch of 1500 tons. The production of the batch was carried out by mixing citrogypsum with a moisture content of 30% and litterless chicken manure with a moisture content of no more than 80% in a ratio of 1:2. The resulting mixture was placed on an open landfill in piles 3 m wide, 1 m high and 400 m long and was mixed twice with a compost turner. Further processing consisted of mixing the mass once every seven days. The controlled parameters were changes in humidity, temperature, pH and nitrogen content during composting. In the course of the experiment, it was found that the introduction of citrogypsum into the composition of the compost helps to optimize the moisture, temperature and pH of the mixture, and a decrease in ammonia emission to 87% was recorded, with an increase in nitrogen content of 2.4 times compared to the initial value. It was concluded that citrogypsum can be used in composting poultry waste to reduce volatilization of ammonia and preserve nutrients.

Keywords: gypsum-containing waste; citrogypsum; chicken droppings; chemical reclamation; nitrogen; ammonia volatilization

1. Introduction

Animal waste is a significant factor that negatively affects the environment. This, in particular, is expressed in the formation of greenhouse gases, an unpleasant odor, the spread of pathogenic microorganisms, etc., which actually worsens the ecological situation [1–5]. Composting is an affordable, efficient and environmentally friendly way to process organic waste using a microbiological method. In the course of biothermal processes, compounds that are easily assimilated by plants are formed in the compost. Compost additives reduce organic matter and nitrogen losses [6–10].

However, the aerobic composting process can cause associated problems; some chemical compounds (for example, trimethylamine (TMA), ammonia (NH3), 2-pentanone, 1-
propanol-2-methyl, dimethyl sulfide, dimethyl disulfide, dimethyltrisulfide and acetophenone) are the causes of unpleasant odor from composting [11–14]. Losses of nitrogen (volatilization of ammonia) that occur during composting of chicken manure can be up to 62% within 1.5–2 months. Volatilization of ammonia during composting is, on the one hand, a negative environmental factor, and on the other hand, it reduces the quality of the resulting fertilizer due to its depletion with nitrogen [3–5]. In general, when using various composting methods, it is necessary to take into account four key aspects—environmental, economic, social and technical, including, among other things, negative factors of the process [15].

The rate of ammonia emission depends on many factors, such as the ratio of carbon to nitrogen in the compost, moisture, aeration, temperature, microbial composition, and composting-optimizing additives. High-temperature composting has become popular for the processing of hardly decomposable organic waste with the participation of thermophilic bacteria, which makes it possible to obtain a safe and effective fertilizer [16].

One of the ways to optimize composting processes is the use of various additives [17] such as biochar [18,19], wood fly ash [20], lime, zeolite [21,22], bentonite [23,24], polyethylene glycol, palm sugar [25], superphosphate [26], microbial inoculants [27], etc. In addition to those listed, gypsum [28,29] and gypsum-containing waste (GCW) [14,26,30,31] are also used as an additive to compost.

GCW with life elements necessary for plants, such as S, Si and Ca, combine well with the organic component of fertilizers and enhance their effectiveness. Chemically, GCW is calcium sulfate dihydrate which has not been subjected to thermal or mechanical stress, which reduces chemical activity; it is especially effective in the decomposition of biomass and has a positive effect on reducing ammonia losses during composting [32].

The likely scheme of the ongoing chemical reactions is as follows:

\[
\text{CaSO}_4 + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4
\]  

Calcium sulphate interacts with ammonia, carbonic oxide (IV), formed as a decomposition product of biomass, in the presence of moisture. This produces ammonium sulfate and calcium carbonate: the first is a valuable mineral fertilizer, and the second helps to stabilize the pH of fertilizers at an optimal level for plants. Calcium and magnesium, which are part of the GCW, are useful as effective soil restoration agents and are recommended by agricultural technicians. This agrotechnical method is based on a decrease the concentration of K and Na cations, which are prone to exchange interactions in saline soils [26,30].

Currently, more than 50 types of gypsum-containing wastes from various industrial enterprises are known [33,34], but flue-gas desulfurization gypsum (FGDG) and phosphogypsum (PG) are the most studied from the point of view of use in agriculture.

At the same time, numerous studies have proven the positive effects of using FGDG and PG and their combinations with other additives in agriculture. In [35], it was found that the addition of 20% FGDG to broiler litter reduces NH\textsubscript{3} evaporation and increases the fertilizer value of broiler litter.

The positive effect of the introduction of FGDG has been proven during the co-composting of dairy manure, sugarcane leaf and press mud (the sludge from sugar factory effluent) [36], a decrease in carbon losses and an increase of mineralization of organic nitrogen in the compost was found. The effect of the FGDG additive on the reduction of nitrogen losses when added into milk manure and solid household waste was also proved [37].

There are results that indicate the possibility of improving the quality of compost through the use of a complex additive consisting of biochar and FGDG [14,38].

According to the data given in [14], the introduction of biochar with FGDG as additional additives to composting of a mixture of slaughter waste, swine slurry and sawdust helps to reduce ammonia volatilization by 26–59%, accelerates decomposition processes, as well as the macro- and micro-nutrient content being enhanced by the supplementation with these co-additives. Positive effects from the introduction of a complex additive into
the compost give accent to a reduction in the duration of the entire process, a decrease in nitrogen and carbon losses, an improvement in the decomposition of lignocellulose and retention of nutrients [38].

The possibility of using phosphogypsum in agriculture has been studied to a greater extent, which is due to the widespread distribution of this gypsum-containing waste throughout the world and large volumes of its annual formation [39,40] which in turn necessitates the search for areas of its utilization, one of which is agriculture.

For example, the authors of [32] proved the positive effect of the introduction of phosphogypsum and superphosphate into the composting of kitchen waste, which is to reduce CH\(_4\) and NH\(_3\) emissions and greenhouse gas emissions well as. Similar results in reducing ammonia and greenhouse gas emissions were obtained when studying the effect of PG and its complex with dicyandiamide on composting sewage sludge [26], as well as during composting in a forced aeration system of pig manure with corn stalks [41]. In addition, as positive effects from the use of PG in agriculture, one can single out an improvement in the physicochemical properties of the soil [42,43] and an increase in productivity due to the presence of useful nutrient elements (Ca, S, P) in its composition [42,44–46].

However, despite the positive effects from the use of PG in agriculture, there are significant environmental risks associated with the content of radioactive elements in its composition (natural uranium radionuclides), which can lead to the possible accumulation of heavy metals and fluorine in soils. A large amount of trace elements in the composition of PG, at certain concentrations, can contribute to the accumulation of toxins in the soil and the transfer of toxic trace elements into water [46,47].

Another gypsum-containing waste that has prospects for use in agriculture is cytrrogypsum (CG), which is formed during the production of citric acid during the microbiological synthesis of molasses using a culture of \textit{Aspergillus niger}, which is grown by a surface or submerged methods.

Molasses is the best raw material for obtaining citric acid; along with a high sugar content, it contains a complex of substances (nitrogen, phosphorus, potassium, etc.) necessary for the life of the fungus, which ensures the maximum yield of citric acid.

A schematic flow diagram of citric acid production is shown in Figure 1 [48].

Unlike natural gypsum, citrogypsum has a high specific surface area, which eliminates the need for additional grinding, and, unlike phosphogypsum, it does not contain harmful impurities that can cause environmental risks [49].

Current information on the effect of CG on ammonia binding in composting animal waste is very limited; therefore, the purpose of this study is to study the effect of the introduction of citrogypsum into the composition of chicken manure on the composting processes in industrial conditions with constant aeration. It is hypothesized that CG, as well as other gypsum-containing wastes (PG, FGDG), the effectiveness of which in agriculture has been proven by numerous studies, will make a positive effect on composting processes.
Figure 1. Basic technological scheme of citric acid production.

2. Materials and Methods

2.1. Raw Materials

As a gypsum-containing component, we used citrogypsum, a by-product of the biochemical synthesis of citric acid (LLC «Citrobel», Belgorod, Russian), which is a powdery material with a specific surface area of about 220–250 m²/kg. The content of CaSO₄·2H₂O in citrogypsum is about 95–97%. According to the data obtained with a scanning electron microscope TESCAN MIRA 3 LMU under the support of Andor software (Oxford Instruments, High Wycombe Buckinghamshire, England) by energy dispersive X-ray spectroscopy, the main elements in citrogypsum are Ca and S (Figure 2) and the predominant oxides are SO₃ and CaO (Table 1). An insignificant amount of Fe, Al and Si oxides can be associated with the presence of soil impurities, as a result of the accumulation and storage of citrogypsum in open dumps.
The organic component was poultry manure from poultry farms that practiced litterless cage keeping of poultry (BEZRK-Belgrankorm, RF). The initial pH of the chicken manure was 5.5, the moisture content was 86% and the content of nutrients for the initial moisture content was: nitrogen (N)–0.5%, phosphorus (P$_2$O$_5$)–1.46% and potassium (K$_2$O)–1.34%.

2.2. Preparation of Raw Materials

The process of accumulation of waste in the waste disposal site of citrogypsum has been carried out for 50 years. The total area of the storage facility is about 58.5 thousand m$^2$.
and the total reserves, according to preliminary estimates, are 351,000.2 m$^3$. The moisture content of waste in its natural state is about 80% by weight. Their sampling from the storage was made by a bucket excavator with subsequent mixing in order to average the material composition. Drying was carried out by periodic stirring in natural conditions in the open air.

For the production of fertilizer, 500 tons of citrogypsum was delivered to the landfill (moisture content no more than 30%) and chicken droppings of cage keeping in the amount of 1000 tons (moisture content no more than 80%).

The experimental batch was 1500 tons. The resulting mixture was placed on an open landfill in piles 3 m wide, 1 m high and 400 m long. Primary kneading was carried out by a front-end loader (Figure 3). The selection of the ratio of the compost component 1:2 by weight (citrogypsum: chicken droppings) was due to the fact that this ratio will provide the optimal value of the N-P-K index after the final mixture is added to the soil horizon of the region in which this experiment was carried out. After combining the components into one pile, double mixing was carried out using a compost turner. Further processing consisted of mixing the mass once every seven days. At the same time, additional homogenization and enrichment of the mixture with oxygen took place to activate aerobic processes.

Figure 3. Heaps with compostable mixture.

To further determine the characteristics of the compostable mixture, point samples were taken and then combined. Samples were taken along the entire length of the collar at five different points at a depth of 50 cm. To determine the volatile chemical ammonia, samples were taken into glass jars with ground-in stoppers, after which they were analyzed immediately upon delivery to the laboratory. The mass of the sample consumed was 1 kg of the compostable mixture.

The determination of the mass fraction of moisture was carried out by the gravimetric method by incubating the samples at a temperature of 100–110 °C for 5 h until a constant mass was obtained.

To measure pH, a weighed portion of the fertilizer from a combined sample weighing 5 g was dispersed in 50 mL of 1 M potassium chloride solution, kept for 15 min, mixed again, and the pH value was measured with an I-160MI ion meter.
The nitrogen content was determined by the Kjeldahl method. To do this, a weighed portion of a compostable mixture weighing 10 g is placed in a flask with a capacity of 500 mL and 200 mL of a solution of hydrochloric acid with a molar concentration of 0.05 mol/L is added. The flask is placed on a liquid shaker and shaken for 30 min. It is allowed to infuse the resulting solution for 12–15 h. The resulting solution is shaken and filtered through a dry folded filter into a flask with a capacity of 500 mL. The contents on the filter are washed with 2–3 portions (30–50 cm each) of a hydrochloric acid solution with a molar concentration of 0.05 mol/L. Next, 30–50 mL of the analyzed solution is poured into the reaction flask of the distillation unit to determine the content of bound ammonia. Next, 30–40 mL of a boric acid solution with a mass fraction of 4% was placed in the receiver, and 3–5 drops of a mixed indicator were added. To the reaction flask, through the funnel of the device, 25–30 mL of sodium hydroxide solution with a mass fraction of 40% was carefully added. The funnel was rinsed with distilled water so that the volume of liquid in the reaction flask was 100–150 mL, after which the funnel valve was closed, the reaction flask was heated, and the solution was brought to a boil. The heating was controlled so that the boiling was quiet. The completeness of the distillation was controlled by the condensate sample with Nessler’s reagent.

In the absence of ammonia, the yellow color of Nessler’s reagent should not appear. The completeness of distillation can be checked using indicator paper (pH 6–7). After the end of the distillation, the receiver was disconnected, the bubbler was washed with distilled water, collecting the wash water in the receiver, and the content of the receiver was titrated with a solution of sulfuric acid with a molar concentration of 0.05 mol/L until the green color changed to raspberry.

The ammonium and nitrate forms of nitrogen were determined by the colorimetric method. The main part of ammonium nitrogen in the soil is in the absorbed or exchangeable condition and is easily displaced from the soil adsorption complex (SAC) by other cations (for example, potassium).

\[
(SAC)NH_4^+ + KCl \rightarrow (SAC)K^+ + NH_4Cl
\]  

(2)

The formed ammonium chloride when interacting with Nessler’s reagent in an alkaline medium (K$_2$HgI$_4$) forms a yellow complex compound–ammonium iodide mercurate (NH$_2$Hg$_2$OI). The intensity of the color obtained is proportional to the ammonium content in the solution.

\[
NH_4Cl + 2K_2HgI_4 + 4KOH \rightarrow NH_2Hg_2OI + 7KI + KCl + 3H_2O
\]  

(3)

To eliminate the influence of Ca$^{2+}$ and Mg$^{2+}$ cations, which interfere with the determination, a Rochelle salt solution (potassium-sodium tartrate KNaC$_4$H$_4$O$_6$·4H$_2$O) is added to the analyzed sample. The optical density of the solution is determined on a photocolorimeter or spectrophotometer at a wavelength of 440 nm (blue filter). Inorganic nitrogen NH$_4^+$, NO$_3^-$ and NO$_2^-$ were determined by extraction using 2 mol/L KCl and then analyzed using a Unico 2100 spectrophotometer operating in the visible region of the spectrum (325–1000 nm). The analysis method is photometric.

The temperature of the composting mixture was recorded by a DS18B20 temperature sensor and a TEPLOCOM series data logger.

The measurement of the controlled parameters (humidity, temperature, pH, ammonia volatilization) was carried out every week throughout the composting process for 2 months (56 days), as well as on the 120th day of composting. Straight compost was used as a control.

3. Results and Discussions

3.1. Study of the Effect of CG on the Change in the Moisture Content of Compost

Analysis of the graphs of moisture changes showed that the introduction of citrogypsum into the compost helps to reduce the initial moisture content of the mixture from 86 to
60%, which is due to the lower moisture content of citrogypsum (30%) in comparison with chicken droppings (Figure 4). By the end of the composting process (120 days), the moisture content of the control compost was 60%, compost with the addition of CG amounted to 42% and the total moisture loss from the initial one was 14 and 18%, respectively.

![Figure 4. Changes in moisture content during composting.](image)

The moisture content in compost is of great importance for the course of microbiological processes. Decomposition processes proceed much faster in thin liquid films that form on the surface of organic particles. The nature of the particles and their size affect the value of the optimum moisture content. The most acceptable is the moisture content in the compost in the range of 50–60%, with a moisture content of less than 30% of the total mass, the rate of biological processes significantly decreases, and with a moisture content of 20%, they can completely stop. At the same time, at a humidity of more than 65%, air diffusion may decrease, which in turn contributes to a significant reduction in degradation and is accompanied by stenches. If the moisture content is too high, the voids in the compost structure are filled with water, which limits the access of oxygen to microorganisms [50–52].

Thus, the introduction of citrogypsum optimizes the initial moisture content of the compost and contributes to its smoother decrease throughout the entire period of the composting process. Moisture readings are maintained at the optimum level throughout the composting period. The control sample is characterized by slight jumps in humidity over time, which can be explained by the negative influence of the initial humidity of the control compost on air diffusion.

The similarity of the profile of the graphs of the decrease in humidity indicates that the addition of GCW does not affect the intensity of the change in the controlled indicator.

### 3.2. Study of the Effect of CG on the Change in the Temperature of the Compost

The results of the effect of CG on the compost temperature are presented in a graph (Figure 5). The initial temperature in the piles for both types of compost was 20 °C. During the first week, the temperature rise for the control compost was 2 °C, while the temperature of the CG compost increased by 10 °C. A larger increase in temperature may indicate the activation of microbial activity due to the introduction of citrogypsum into the compost, which is compliant with the data obtained by other researchers [53,54].

| Sample        | Days | Standard deviation, % |
|---------------|------|------------------------|
|               | 0    | ±0.2                   |
|               | 7    | ±0.3                   |
|               | 14   | ±0.3                   |
|               | 21   | ±0.3                   |
|               | 28   | ±0.4                   |
|               | 35   | ±0.4                   |
|               | 42   | ±0.1                   |
|               | 49   | ±0.3                   |
|               | 56   | ±0.2                   |
|               | 120  | ±0.3                   |
| Compost+CG    | ±0.2 | ±0.3                   |
| Control       | ±0.3 | ±0.2                   |
|               | ±0.1 | ±0.4                   |
|               | ±0.3 | ±0.3                   |
|               | ±0.2 | ±0.3                   |
|               | ±0.5 | ±0.4                   |
|               | ±0.3 | ±0.3                   |
The tendency of a gradual rise in temperature for both types of compost is common with the flesh until the end of the fourth week (day 28) and reaches 30 °C for non-additive compost and 39 °C for compost with CG. The smooth rise in temperature during the indicated period is explained by the release of heat from the vital activity of bacteria or chemical interaction.

Then, the temperature profile changes. In the control compost by the end of 8 weeks (56 days) the temperature dropped to 24 °C, which indicates the attenuation of the process. At the same time, the compost with CG showed a jumped in temperature from 40 °C in 35 days and to 60 °C on the 49th day. On day 120, the temperature for both types of compost was 20 °C.

It is known that the process of aerobic composting is carried out during several stages or phases, and that each of them is characterized by its own composition of microorganisms.

In the first preparatory phase, microorganisms adapt to the type of waste and habitat conditions. The total population of microbes is still small and the temperature is low.

The second phase is mesophilic. The size of the microbial population increases due to mesophilic organisms adapted to low and moderate temperatures. These organisms break down soluble and easily degradable components such as simple sugars and carbohydrates. The deposits of these substances are quickly depleted, and microbes begin to break down more complex molecules such as cellulose, hemicellulose and proteins. After consuming these substances, microbes secrete a complex of organic acids, which serve as a food source for other microorganisms. However, not all of formed organic acids are absorbed, which leads to their excessive accumulation and, as a result, to decrease in the pH of the medium. pH serves as an indicator of the end of the second stage of composting. However, this phenomenon is temporary since an excess of acids leads to the death of microorganisms [55].

The second phase in our case is observed until the end of the fifth week.

The third phase is thermophilic. The size of the microbial population increases, the general metabolism intensifies and the temperature rises. The mesophilic population is replaced by thermophilic species, which grow at temperatures up to 40–60 °C [52,55]. During this phase, there is an accelerated breakdown of proteins, fats, and complex carbohydrates such as cellulose. After the depletion of food resources, metabolic processes decline, and the temperature gradually decreases. An increase in temperature above this range has a
negative effect on the composting process, which is explained by a decrease in the activity of thermophiles [56]. The introduction of CG in compost helps to optimize composting processes—in the period from 35 to 56 days, an optimal temperature is created at which the death of mesophilies occurs and thermophiles come to replace them, which raises the temperature to 60 °C. The duration of the period (more than 14 days) at which the temperature was kept above 55 °C gives grounds to conclude that the introduction of CG into the compost contributes to the creation of conditions under which the death of pathogenic microorganisms and weed seeds is ensured—the process of compost bio-sterilization [14,57]. It should be noted that the maximum temperature of the control sample was 30 °C, which indicates the absence of a thermophilic phase as such.

The fourth phase is a return to mesophilic conditions. The organic substances remaining as a result of the thermophilic phase form humic complexes. In our case, the fourth phase begins by the end of the 2nd month and on the 120th day, biological processes and, as a result, temperature changes completely fade, the temperature of both types of compost becomes equal to the ambient temperature.

Thus, the introduction of CG into compost contributes to the optimization of composting processes—in the period from 35 to 56 days, an optimal temperature is created at which the death of mesophilies occurs and thermophiles come to replace them, which raises the temperature to 60 °C. The duration of the period (more than 14 days) at which the temperature was kept above 55 °C allows us to conclude that the introduction of CG into the compost ensures the creation of conditions leading to the death of pathogenic microorganisms and weed seeds—the process of compost bio-sterilization [14,57].

3.3. Study of the Effect of CG on the Change in the pH of Compost

In their studies, Singh etc [58] note that the optimal pH range of the compost mass, at which optimal conditions for anaerobic digestion are provided, is in the range of 6.8 to 7.2, while Chan notes [59] that a pH range of 7 to 8 is optimal for composting.

The pH of citrogypsum and chicken droppings used in this experiment amounts to 5.5.

The change in the pH of the compost with CG and the control sample is shown in Figure 6. In the case of the control compost there is an inverse dependence of pH on temperature (Figure 5).

According to the above data, it can be seen that with the introduction of CG, the pH of the compost increases up to 14 days and reaches 6.5; this is due to the more intense release of ammonia, that leads to an alkaline reaction, and after that the pH is stabilized. During 14–35 days, an increase in pH is observed, that is due to the intensification of decomposition processes. In 35 days the thermophilic phase is started and a decrease in pH is observed, which is most likely associated with the formation of low molecular weight organic acids and CO₂, evaporation of ammonia and nitrification during composting. It should be noticed that the introduction of CG into the compost ensures the maintenance of the pH of the mixture in the required, previously indicated [58,59] optimal range during the entire composting process.

For the control compost, the pH values practically did not change during the entire process. The maximum pH values were recorded at the 8th week of the process and amounted to 5.8. Low pH values of the control compost may indicate a little biological activity.
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3.4. Study of the Effect of CG on Ammonia Volatilization

As previously stated, ammonia emissions are the main cause of nitrogen loss during composting, which leads to a decrease in compost quality and environmental risks in full-scale composting facilities [12–14].

Figure 7 shows graphs of changes in nitrogen content (Figure 7a) including in terms of dry matter (Figure 7b). In the compost with cytrogypsum, a stable increase in nitrogen was recorded, from 2% (beginning of the experiment) to 4.83% (120 days), while in the control compost, the nitrogen content decreased from 3.57% to 2.35%, respectively (Figure 7b).

In addition to fixing the dynamics of total nitrogen throughout the entire period of the experiment, at the end of the experiment on the 120th day, the content of ammonium nitrogen was determined. It is thanks to ammonium nitrogen that the process of immobilization of nitrogen in the mixture occurs (the transformation of mineral forms of nitrogen by microorganisms into organic substances of microbial cells and metabolites). The content of ammonium nitrogen for 120 days for compost without cytrogypsum was 0.17% for the initial moisture content, and for compost with cytrogypsum 0.92% for the initial moisture content.

Based on the result of the amount of nitrogen in the composting mixture, the total ammonia emission during composting with citrogypsum was significantly less during aeration than during composting without citrogypsum, which is consistent with the data from studies using FGDG [37]. The highest NH₃ volatilization rate in the present study was at temperatures above 50 °C (Figure 5). Probably, according to the inhibition of the nitrification process [60], high temperature affects the volatilization of ammonia.

The process, which comes to the end of volatilization of ammonia, can be divided into three parts:

- some of the organic nitrogen is first decomposed to some simple N− containing compounds and stored in compost. These compounds are mineralized after biodegradation slowdown;
- slowly decomposing fraction with a high content of biodegradable nitrogen has been mineralized;
NH$_4^+$ after ammonification, in the process of biomass remineralization had influenced the NH$_3$ emission.

![Figure 7](image-url)

**Figure 7.** Change in nitrogen content during composting. (a)—nitrogen content to original moisture; (b)—nitrogen content in terms of dry mass.

However, it should be considered that citrogypsum has the ability to absorb ammonia and, even at high temperatures, the percentage of its volatilization is minimal. Further, the addition of citrogypsum reacted [61] ammonium carbonate to ammonium sulfate with the subsequent formation of calcium carbonate. Nitrogen in the form of ammonium carbonate, unlike ammonium sulfate, tends to volatilize. During the study, it was noted that the addition of citrogypsum reduced NH$_3$ volatilization by 76.45% compared to compost without additives. According to the results of other studies [14], aluminum sulfate, chloride salts of aluminum, calcium and magnesium, FGDG and sodium bisulfate reduce NH$_3$ volatilization by 0–87%, depending on the rate and intervals of incubation of bacteria.
After the ammonification process, under the influence of other microorganisms—nitrifiers—occurs, or so-called nitrification—the oxidation of ammonia into nitric acid. The nitrification process takes place in two stages: the oxidation of ammonia to nitrous acid and the transition of nitrous acid to nitric acid. The first stage is due to the vital activity of bacteria of the genera Nitrosomonas, Nitrosocystis, Nitrosolobus and Nitrosospira.

The transformation of a positively charged \( \text{NH}_4^+ \) cation into an \( \text{NO}_2^- \) anion promotes acidification of the medium, thereby increasing the solubility of a few compounds. Nitrifiers of the second phase—bacteria of the genera Nitrobacter, Nitrospira and Nitrococcus—make the oxidation of nitrite ion into nitrate ion. Then nitric acid combines with the bases of the soil and forms salts—nitrates. The dynamics of the nitrification process in compost depends on weather conditions, on the composition of the compost, its dispersion, aeration, humidity and degree of homogeneity and varies greatly over time.

The field of attenuation of biological processes of nitrification and denitrification, the course of which is accompanied by an increase in temperature (Figure 5) and a change in pH (Figure 6), the active phase of ammonia emission begins, in our case after 56 days. Usually this phase is accompanied by the release of an unpleasant odor and negative impact on the atmospheric air [1–3]. However, the introduction of citrogypsum into the compost makes it possible to bind the released ammonia according to the Formula (1), which explains the increase in the nitrogen content in the compost (Figure 7b). At the same time, the process of emission of ammonia into the atmosphere continues in the control compost, as evidenced by a decrease in nitrogen indicators in its composition.

Thus, in comparison with the control sample, in which the nitrogen content during the experiment decreased by 1.5 times (when converted to dry matter), compost with cytogypsum will have a higher nutritional value and lower emissions of harmful substances into the atmosphere, as evidenced by an increase nitrogen content 2.4 times by the end of the experiment (Figure 7b).

The data on ammonium nitrogen, the content of which in the compost with CG by the end of the experiment (day 120) was 5.4 times higher than in the control composition, also confirm the effectiveness of the addition of citrogypsum in composting chicken manure.

4. Conclusions

Based on the results of a technological experiment in the field, it can be concluded that the use of citrogypsum as a compost component is effective. The introduction of citrogypsum into the composition of the compost helps to optimize the moisture, temperature and pH of the mixture, which has a beneficial effect on the course of the composting process. The addition of citrogypsum helps to reduce ammonia emissions and the emission of harmful substances into the atmosphere during the entire period of composting of litterless chicken manure, as well as the accumulation of ammonia nitrogen and increase the nutritional value of the compost mixture.

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