Study on pollutant characteristics of different types of manure sludge drying condensate

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Abstract. In order to further study the characteristics of condensate contaminants generated during the drying of livestock manure and biogas residues, the three biogas residues were dried at different temperatures and at different time. The condensate produced in the experiment was collected and its pH, ammonia nitrogen and COD were measured. Exploring the effects of different temperatures and different times on the characteristics of condensate contaminants during the drying of manure sludge. And further comparing the characteristics of different types of biogas residue dry condensate. The results show that: the three biogas residue condensates are weakly alkaline; the three biogas residue condensates COD rises with the increase of drying temperature, the use of low temperature drying can reduce the organic content of the dry condensate; low temperature drying can significantly reduce Exhaust gas treatment load to prevent the loss of organic fertilizer efficiency; with the extension of the drying time, the NH₃-N content of the dry manure biogas residue dry condensate increased; comprehensive consideration of drying efficiency and drying for the characteristics of condensate. It is recommended that all three kinds of biogas residues be dried at 60°C at low temperature.

1. Introduction

The total amount of livestock and poultry manure in China is as high as 20.08×10⁸t [1]. The use of anaerobic fermentation technology to use these manures as raw materials for biogas projects is of great significance for the realization of manure recycling. At the same time, the production volume of the fermentation product biogas residue is also huge. The biogas residue liquid contains about 90% of water, which is very large in volume and very inconvenient for storage and transportation. Studies have shown that [2-3], the transportation cost of biogas residue and the ease of use are important factors that affect farmers' willingness to use. Therefore, the biogas residue needs to be dried for subsequent further use. However, in the drying process, the biogas residue not only removes water, but also releases some harmful volatile substances [4], such as volatile organic compounds and NH₃-N. Soluble volatile substances are dissolved in water to form a dry condensate with complex composition. If these condensates flow directly into the environment without proper treatment, they will easily cause environmental pollution.

2. Experimental materials, devices and methods

2.1 Experimental materials
The experiment selected biogas residue after anaerobic fermentation of pig manure, cow manure and chicken manure as the research object. Among them, pig manure biogas residue was taken from the biogas project in Minsheng Village, Chongming District, Shanghai; cow manure biogas residue was taken from the biogas project of Xidi Dairy Farm in Pudong New District, Shanghai; chicken manure biogas residue was taken from a biogas in Longwang Township, Funan County, Anhui Province. The slag discharge port of the project site. The above materials are separated by solid-liquid separation. When not in use, the experimental materials are placed in a low-temperature refrigerator and sealed at 4°C. Through testing, the raw material characteristics of the following types of biogas residues are obtained.

| Types          | pH     | Total nitrogen (g kg⁻¹ DM) | NH₃-N (g kg⁻¹ DM) | COD (g kg⁻¹ DM) |
|----------------|--------|----------------------------|-------------------|-----------------|
| Pig manure     | 8.136  | 32.3                       | 5.00              | 55.01           |
| Cow dung       | 7.535  | 13.5                       | 0.40              | 33.25           |
| Chicken manure | 8.241  | 39.1                       | 6.14              | 69.50           |

2.2 Experimental device
This article draws on the literature [5-9] sludge drying condensate collection experimental device, and improve the biogas residue dry condensate collection experimental device shown in Figure 1.

2.3 Experimental method
In the experiment, weigh about 60g of the manure sludge sample, lay it flat on the bottom of the reactor, wait for the oil bath to heat up to the set temperature, connect the experimental device as shown in Figure 1, after checking the error, start the micro-circulation pump. The biogas residue is dried and the condensate in the drying process is collected. After the drying is completed, the condensate in the triangular suction filter flask is transferred to a sampling bottle and stored at 4°C, and its pH, NH₃-N content and COD are measured as soon as possible.

2.3.1 Effect of drying temperature on the characteristics of condensate
In order to study the characteristics of condensate contaminants at different drying temperatures under low temperature conditions and manure sludge, four drying temperatures of 50, 60, 70, and 80 °C were set (40 °C drying is extremely slow, and the temperature is low, the oil bath The ability to maintain a constant temperature is poor, so this experiment will not study it). In order to further compare the characteristics of the condensate between low-temperature drying and high-temperature drying, and to
verify the superiority of low-temperature drying over high-temperature drying in terms of volatile emissions, two high-temperature experiments at 120 and 140°C were set for comparison.

2.3.2 Effect of drying time on the characteristics of condensate
In order to study the effect of drying time on the characteristics of biogas residue dry condensate under low temperature conditions, the biogas residue was dried at a fixed temperature at 60 °C, and the micro circulation pump was suspended every 3 hours, the triangular suction filter flask was replaced, and the dry condensate was collected. After the experiment, the pH value, NH3-N content and COD of the dried condensate collected at different times were measured respectively.

2.4 Test methods
pH value: directly measured by glass electrode method; determination of total nitrogen: digested by sulfuric acid-hydrogen peroxide, Kjeldahl method. Determination of NH3-N: using Nessler's reagent ultraviolet spectrophotometry; COD measurement; using rapid digestion colorimetry, the specific method is: take an appropriate amount of biogas residue into a solution of moderate concentration, and determine the COD value of the clear solution after centrifugation. And the soluble COD value of biogas residue is calculated from this. The above analysis methods refer to "Water and Wastewater Monitoring and Analysis Methods" [10].

3. Experimental results and analysis
3.1 Changes in pH of manure sludge drying condensate at different drying temperatures
The pH changes of the dried condensate obtained from the three biogas residues under different drying temperature conditions are shown in Figure 2. It can be seen from the figure that the three kinds of biogas residue condensate are weakly alkaline and have little change. The pH of the dried condensate of pig manure, cow manure, and chicken manure is between 8.5-9.1, 7.5-8.5, and 8.9-9.4. As the drying temperature increased, the pH of the three condensate drying condensates showed a slight decrease first and then increased. By comparing the dry condensate of biogas residue under high temperature conditions of 120 and 140°C with the four low temperature groups of 50-80°C, it was found that the pH of the dry condensate of pig manure biogas residue and chicken manure biogas residue was higher than that of low temperature group. The pH of the dry condensate in the cow dung biogas residue in the high temperature group was not significantly different from that in the low temperature group. At the same temperature, the pH values of the three kinds of biogas residue dry condensate from low to high are: cow manure biogas residue<pig manure biogas residue<chicken manure biogas residue.

Figure 2. The pH change of condensate under different drying temperature

3.2 Changes of COD of manure sludge drying condensate at different drying temperatures
The change of COD of three kinds of biogas residues under different drying temperature conditions is shown in Figure 3. It can be seen from the figure that with the increase of the drying temperature, the
COD of the three biogas residue drying condensates all show an upward trend, but not the same amplitude. When the temperature is low, the COD is at a low level and the rise rate is slow. When the temperature reaches a certain value, it increases rapidly. The temperature values at the point of inflection of the COD values of the three biogas residue condensates of pig manure, cow manure and chicken manure were 70℃, 80℃ and 70℃, respectively, and the corresponding points were 85.76, 72.83 and 129.95 mg/L. At 60℃, the COD of the three biogas residue condensates of pig manure, cow manure and chicken manure was 74.08, 43.67, 126.04 mg/L respectively, and reached the maximum at 140℃, respectively 534.67, 307.40, 602.61 mg/L, respectively 7.22, 7.04, 4.78 times at 60 ℃. The three kinds of biogas residues have different CODs at the same temperature. The overall volume of chicken manure biogas residue > pig manure biogas residue > cow manure biogas residue.

Figure 3. COD changes under different drying temperature conditions

By comparing the COD of manure sludge drying condensate under high temperature conditions of 120 and 140℃ with 4 low-temperature groups of 50~80℃, it was found that the COD of low-temperature drying condensate was significantly lower than that under high-temperature conditions, and drying at high temperature The increase in condensate COD is higher than that in the low temperature range. Therefore, the use of low-temperature drying biogas residue can effectively reduce the content of organic matter in the condensate.

3.3 Changes of NH3-N content in drying condensate of manure sludge biogas residues at different drying temperature

The change of NH3-N content in the dried condensate of three biogas residues under different drying temperatures is shown in Figure 4. It can be seen from the figure that as the drying temperature increases, the NH3-N content of the pig manure residue dry condensate first decreases and then increases, reaching a minimum value of 573.75 mg/L at 60 ℃, at a low temperature stage (50-80 ℃), at 80 ℃ The maximum value is 752.68 mg/L. When the temperature is further increased, the NH3-N content in the condensate increases rapidly, reaching 1103.78 mg/L at 140℃, which is about twice the minimum value. The NH3-N content of cow manure biogas residue dry condensate showed a downward trend as the temperature increased. It reached a maximum of 188.89 mg/L at 60℃ and a minimum of 97.73 mg/L at 80℃. When the temperature increased from low to high temperature, There was a slight increase, which was stable at about 110 mg/L. The NH3-N content of the dried condensate of cow dung biogas residue at different temperatures was always at a low level. The content of NH3-N in the dried condensate of chicken manure biogas residue shows an upward trend with increasing temperature. The lowest value is 5086.62 mg/L at 50℃, and it is stable at 70-80℃ at a low temperature (50-80℃), about 3000 At about mg/L, when the temperature further increases, the NH3-N content of the condensate continues to increase, reaching 4202.27 mg/L at 140℃, which is 1.56 times the minimum value.
The three kinds of manure sludge dry condensate must be treated before they can be discharged, especially pig manure and chicken manure. The three different biogas residues have different NH3-N content at the same temperature. The overall volume of chicken manure biogas residue > pig manure biogas residue > cow manure biogas residue. By comparing the NH3-N content of biogas residue dry condensate under high temperature conditions of 120 and 140℃ with 4 low temperature groups of 50 ~ 80℃, it was found that the NH3-N content of pig manure biogas residue and chicken manure biogas residue low temperature group was lower than high temperature Group, and the NH3-N content in the dried condensate of cow dung biogas residue is relatively higher in the low temperature group than in the high temperature group.

3.4 Changes in pH of manure sludge drying condensate at different drying time

Under the condition of 60℃, the pH changes of the dry condensate of the three kinds of biogas residues at different drying times are shown in Figure 5. It can be seen from the figure that with the extension of the drying time, the pH value of the condensate is relatively stable, showing weak alkaline. The pH values of three biogas residue condensates of pig manure, cow manure and chicken manure were maintained at 8.5-8.8, 7.4-8.4 and 9.0-9.4, respectively. The pH values of the three kinds of biogas residue dry condensate are chicken manure biogas residue > swine manure biogas residue > cow manure biogas residue.

3.5 Changes of COD of manure sludge drying condensate in different drying time

At 60℃, the COD changes of the three condensate residues with different drying times are shown in Figure 6. It can be seen from the figure that with the extension of the drying time, the COD of pig manure biogas residue dry condensate does not change much, fluctuating between 60.81 and 99.59
mg/L, and maintains a low level. The COD of cow manure biogas residue dry condensate first decreased and then increased. The maximum value was 83.96 mg/L at 3 hours, and the minimum value was 71.03 mg/L at 6 hours, and then slowly increased. The COD of chicken manure biogas residue drying condensate showed an upward trend with the extension of drying time, increasing from 95.38 mg/L to 153.40 mg/L.

**Figure 6. COD change of condensate at different drying time at 60℃**

3.6 Changes of NH3-N content in drying condensate of manure sludge residue at different drying time

Under the condition of 60℃, the change of NH3-N in the dry condensate of three kinds of biogas residues with different drying time is shown in Figure 7. It can be seen from the figure that with the extension of the drying time, the NH3-N content of the pig manure biogas residue dried condensate showed a downward trend. The dried ammonia condensate in the first 3 h had the highest NH3-N concentration, reaching 803.32 mg/L. After that, the NH3-N content decreased rapidly and remained at Fluctuation around 450 mg/L. The NH3-N content of the cow manure biogas residue dry condensate gradually increased with the extension of the drying time, which was only 80.85 mg/L at 3 h and reached a maximum of 283.41 mg/L at 12 h, but it was always at a low level. The NH3-N content of the dried condensate of chicken manure biogas residue decreased with the extension of drying time, from 3 h to 12 h, the NH3-N content decreased from 3969.50 mg/L to 1565.78 mg/L.

**Figure 7. Changes of NH3-N in condensate at different drying time at 60℃**

4. Conclusion

(1) Under the experimental temperature conditions, the three kinds of biogas residue dry condensate are relatively stable and weakly alkaline. At the same temperature, different types of biogas residues have different pH, and from low to high are cow manure biogas residue, pig manure biogas residue, and chicken manure biogas residue.

(2) The COD of the three types of biogas residue drying condensate rises with the increase of drying temperature, and the increase in the high temperature stage is greater than that in the low temperature stage. At 60℃, the COD of the three biogas residue condensates of pig manure, cow
manure and chicken manure was 74.08, 43.67, 126.04 mg/L respectively, and reached the maximum at 140℃, respectively 534.67, 307.40, 602.61 mg/L, Respectively 7.22, 7.04, 4.78 times at 60 ℃. The three kinds of biogas residues have different CODs at the same temperature. The overall volume of chicken manure biogas residue > pig manure biogas residue > cow manure biogas residue. Therefore, the use of low temperature drying can reduce the organic content of the drying condensate.

(3) As the drying temperature increases, the NH3-N content of the pig manure biogas residue condensate first decreases and then increases, reaching a minimum value of 573.75 mg/L at 60℃ and a maximum value of 1103.78 mg/L at 140℃, which is about 2 times the minimum value. The NH3-N content of the cow manure biogas residue dry condensate showed a downward trend as the temperature increased, reaching a maximum value of 188.89 mg/L at 60℃ and a minimum value of 97.73 mg/L at 80℃. The nitrogen loss rate caused by NH3-N volatilization remained basically at Below 5%. The NH3-N content in the dried condensate of chicken manure biogas residue showed an upward trend with increasing temperature. The minimum value was 5086.62 mg/L at 50℃, and the maximum value was 4202.27 mg/L at 140℃, which was 1.56 times the minimum value. The three different biogas residues have different NH3-N contents at the same temperature. The overall volume of chicken manure biogas residue > pig manure biogas residue > cow manure biogas residue. No matter high temperature drying or low temperature drying, the exhaust gas needs to be purified, but low temperature drying can obviously reduce the exhaust gas treatment load and alleviate the loss of organic fertilizer efficiency.

(4) The pH of the dry condensate of the three biogas residues at different drying times all showed stable weak alkaline, and there was no obvious change with the extension of the drying time.

(5) The COD of pig manure biogas residue dry condensate at different times is always at a low level and does not change much, fluctuating between 60.81 ~ 99.59 mg/L. The COD of cow manure biogas residue dry condensate at different drying times first decreases After the increase, but the overall level is also low, between 71.03 ~ 83.96 mg/L, the change range is small, the COD of chicken manure biogas residue dry condensate increases with the extension of the drying time, increasing from 95.38 mg/L To 153.40 mg/L.

(6) With the extension of the drying time, the NH3-N content of the dried condensate of pig manure and chicken manure sludge decreased, the pig manure biogas residue decreased from 803.32 mg/L to about 450 mg/L, and the chicken manure biogas residue from 3969.50 mg/L decreased to 1565.78 mg/L, and the NH3-N content of the dried condensate of cow dung biogas residue increased from 80.85 mg/L to 283.41 mg/L, but it was always at a low level.

(7) Considering the drying efficiency and drying condensate characteristics comprehensively, it is recommended that all three kinds of biogas residues should be dried at 60℃ at low temperature.

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