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Manure digestate storage under different conditions: Chemical characteristics and contaminant residuals

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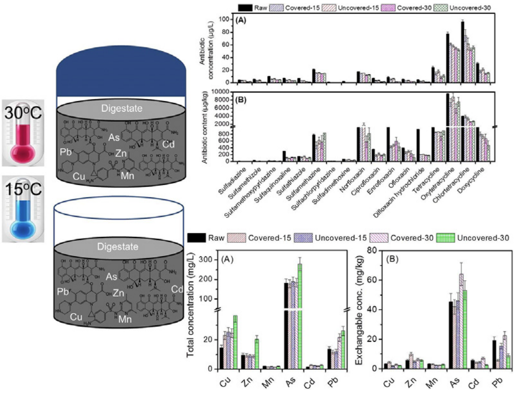
HIGHLIGHTS

- Openly storing digestate at high temperature altered its chemical characteristics.
- Chemical characteristics changed slightly when stored digestate with coverage.
- Antibiotic residues decreased & heavy metals were enriched during digestate storage.
- Residual of quinolones and tetracyclines was still notable after digestate storage.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, chemical characteristics and contaminant residuals in livestock manure digestate were investigated during storage under different conditions. Results show that storing digestate openly under the mesophilic condition (30 ± 1 °C) led to water evaporation and thus considerable mass reduction. As a result, concentrative effect occurred to increase the contents of organic matter, nutrients, and heavy metals during digestate storage. By contrast, ammonium (NH_4^+) concentration in digestate decreased over storage period. The concentrative effect and NH_4^+ reduction could be mitigated by storing digestate with coverage and/or under psychrophilic conditions (e.g. 15 ± 1 °C). Regardless of storage conditions, organic matter was further biodegraded, thereby reducing the residuals of antibiotics in digestate. Antibiotic removal was more notable when digestate was stored under mesophilic conditions. Nevertheless, additional processes to control heavy metals and antibiotics in digestate are still necessary before agricultural applications.

1. Introduction

Anaerobic digestion has been well established for the treatment of livestock manure, which is a vexing issue to the environment due to global development of intensive livestock farming (Mao et al., 2015). By anaerobic digestion, livestock manure can be effectively converted into two valuable products, namely biogas and digestate. Biogas, as a renewable energy, can be combusted for the supply of heating and electricity as well as be upgraded for high value applications, such as vehicle fuel (Zaks et al., 2011). Digestate can be employed as organic fertilizer for agronomic activities given its high nutrient contents (Nkoa, 2013).

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Despite its well-known agronomic values, the application of digestate as organic fertilizer or soil amendment to farmlands replies on the seasonality of plant and crop growth. Both organic and mineral fertilizers can result in severe environmental concerns, for example, via nutrient leaching and runoff into ground and surface water, when used during fallow period and/or when crops and plants exhibit minimal nutrient uptake (e.g. in autumn and winter) (Paavola and Rintala, 2008; Perazzolo et al., 2017). On the other hand, digestate is produced continuously from anaerobic digestion of livestock manure and other substrates, such as crop stalks and organic fractions of municipal solid wastes (Mao et al., 2015). Moreover, biogas plants in some regions are surrounded by limited farmlands, thus, long-distance transportation of digestate is necessary. As a result, digestate has to be stored onsite for a certain period (up to 10 months) before favorable agronomic applications in adjacent or remote farmlands (Hansen et al., 2006; Paavola and Rintala, 2008).

Digestate can be stored in the open and closed reservoirs after solid-liquid separation or not. Regardless of storage conditions, gaseous emissions occur from digestate, thereby reducing its nutrient contents and compromising the environmental benefits of anaerobic digestion for the management of livestock manure. For instance, Menardo et al. (2011) reported that methane (CH_4) yields were heterogeneous in the range between 2.88 and 37.63 normal liters per kilogram of volatile solids (NL/kg VS) during the open storage of digestate. The CH_4 production during digestate storage was determined by the organic loading rate and quality of feedstock to the anaerobic digestion system. Similar results were also reported by Gioelli et al. (2011) who demonstrated that biogas production during the storage of digestate and its liquid fraction after mechanical separation was linearly related to the ambient temperature. Moreover, ammonia (NH_3) volatilization is considerable during digestate storage, particularly in summer given its high ammonium (NH_4^+) content and alkalinity (Sommer, 1997; Holly et al., 2017). Thus, strategies, such as acidification (Regueiro et al., 2016) and advanced coverage systems (Balsari et al., 2013), have been recommended to minimize and/or capture gases emitted from digestate during storage. With coverage systems, CH_4 produced during digestate storage can be recovered to enhance the biogas yield of anaerobic digestion plants (Menardo et al., 2011).

Compared to gaseous emissions, investigation on the variation of digestate characteristics during storage is rather scarce. In particular, little is known about the residues of heavy metals and antibiotics in digestate during storage. Heavy metals and antibiotics are intensively used to improve livestock growth and productivity (Heuer et al., 2011; Wang et al., 2013). Given their over-dosage and low assimilation via livestock metabolism, heavy metals and antibiotics largely remain in excretes, thereby challenging the manure treatment and subsequent farmland applications. Indeed, manure-related organic fertilizer has been considered as an important source of heavy metals and antibiotics as well as their resistant genes in the environment, particularly the soil ecosystem (Knapp et al., 2010; Kupper et al., 2014). Although the residual of heavy metals in digestate is commonly lower than the threshold of relevant national standards, they can accumulate in farmlands over long-term digestate application (Nkoa, 2013). Thus, understanding the dynamics of heavy metals and antibiotics during digestate storage is of significance to evaluate its quality for environmental-friendly agronomic applications.

In this study, livestock manure digestate was stored hermetically and openly under psychrophilic and mesophilic conditions, respectively, to stimulate the scenarios in practice. Chemical characteristics of digestate were evaluated under different storage conditions. Dynamics of heavy metals and antibiotics during digestate storage were also elucidated. Results from this study provide unique insight to the management and application of manure digestate.

2. Materials and methods

2.1. Manure digestate

Manure digestate was collected from a continuous stirred tank reactor at a local commercial pig farm (Beijing, China). The digester feedstock consisted of 90% pig slurry and 10% corn silage. There was no separation treatment after anaerobic digestion. Basic physiochemical properties of fresh digestate were measured in triplicates according to the analytical methods described in Section 2.3. Specifically, the digestate contained 28.8 ± 3.2 g/L total chemical oxygen demand (COD), 6.4 ± 0.33 g/L total nitrogen (TN), 4.5 ± 0.23 g/L NH_4^+, 0.51 ± 0.14 g/L total phosphorus (TP), 40.7 ± 0.2 g/L total solids (TS), and 22.9 ± 0.2 g/L volatile solids (VS). The pH and electrical conductivity of the digestate were 8.04 ± 0.04 and 23.5 ± 0.6 mS/cm, respectively.

2.2. Experimental protocol

Manure digestate was stored under different laboratory conditions to simulate those in practice. Four treatments were performed by storing 2 L manure digestate into amber glass bottles with or without coverage under psychrophilic (15 ± 1 °C) or mesophilic (30 ± 1 °C) condition for two months. Specifically, two treatments, namely *covered-30* and *uncovered-30*, were stored at the mesophilic temperature with and without coverage, respectively. Similarly, the other two treatments at the psychrophilic temperature were denoted as *covered-15* and *uncovered-15*, respectively. A Tadler sampling bag was connected with glass bottles that were tightly sealed to allow for gaseous release. Each treatment was conducted in triplicates. Mixed liquor samples were collected weekly from the four treatments for analysis.

2.3. Analytical methods

TS and VS were measured based on the standard method 2540. COD was analyzed by the fast digestion spectrophotometric method with high range COD vials (HACH, USA). TN and TP were determined by the alkaline potassium persulfate digestion-UV spectrophotometric method and the ammonium molybdate spectrophotometric method, respectively. NH_4^+ and NO_3^- were measured using a flow injection analysis system (QuikChem 8500, Lachat, CO). An Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA) was used to measure the mixed liquor pH and electrical conductivity.

At the beginning and conclusion of digestate storage, mixed liquor samples were centrifuged at 3750*g* for 20 min to analyze the concentrations of soluble heavy metals and antibiotics in both the solid and liquid fractions of digestates. Soluble/exchangeable heavy metals in the solid fraction of digestates were extracted by adding acetic acid based on the sequential extraction method reported by Mossop and Davidson (2003). Key heavy metals, including copper (Cu), zinc (Zn), manganese (Mn), arsenic (As), cadmium (Cd), and lead (Pb), were analyzed by an inductively coupled plasma-optical emission spectrometry (710 ICP-OES, Agilent Technologies, CA).

In this study, 17 compounds belonged to three groups of widely used antibiotics, namely sulfonamides, quinolones, and tetracyclines, were analyzed based on the analytic method previously reported by Liu et al. (2018). Key physiochemical properties of the 17 antibiotics are shown in Table S1, Supplementary data. Briefly, the analytical method consisted of solid phase extraction (SPE), derivatization, and quantification by an ultrahigh performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS, Waters, Milford, MA). To avoid the interference of metals and thus improve the extraction of antibiotics, 0.6 g ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) was added to each 400 mL liquid sample. Solid samples after freeze-dry were grounded to powder and then