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Ammonia recovery from anaerobic digester effluent through direct aeration

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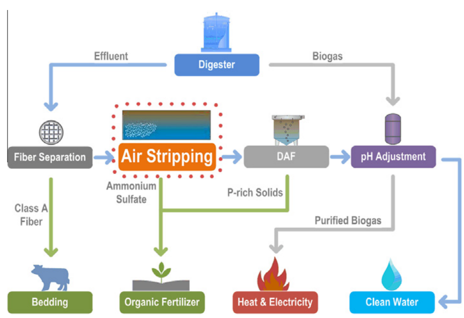
HIGHLIGHTS

- Solely injecting air into digester effluent can elevate pH and remove ammonia.
- Smaller bubble size favors the process.
- Carbonate and ammonium concentrations first increase then decrease during aeration.

GRAPHICAL ABSTRACT



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ABSTRACT

A direct aeration strategy was developed for ammonia recovery without alkali addition. The main chemical buffer system of digested effluent is made up of high concentration of acidic species, which lead to a hypothesis that elevation of pH for ammonia release could be achieved by removing supersaturated CO_2, dissolved carbonate, and bicarbonate solely. The concept was tested in lab scale reactors with digested dairy manure focusing on temperature, bubble size, liquid depth and airflow rate. It has demonstrated that simple air stripping without alkali chemical input is an effective way to elevate pH of the digested effluent due to intriguing chemical shifts strongly related to the high levels of carbon dioxide, bicarbonates and carbonates present in digested effluent. These chemical shifts, ultimately release carbon dioxide and raise the pH of the effluent to levels near 10, which with combined elevated operating temperatures from waste engine heat, can lead to 70–90% shift from ionic to free, gaseous form of ammonia and subsequent recovery of ammonia through acid contact. The chemical relationships and equilibrium shifts associated with the aeration process and its subsequent release of gases were further investigated by chemical equilibrium model.

1. Introduction

Farm-based anaerobic digestion (AD) systems offer multiple benefits such as renewable energy, methane destruction, carbon avoidance, and value-added production of digested fibrous solids [1]. These systems typically produce a nutrient-rich effluent that still requires proper disposal to land, with large animal operations producing voluminous amounts of wastewater that hold potential for overloading nearby soils with excess nitrogen and phosphorous [2]. Technological responses to these nutrient concerns has simultaneously grown in interest, with particular attention tuned to the development of nitrogen technologies that can either, alone or in series with AD, reduce nitrogen content in the wastewater [3]. An AD research focus has been on ammonia recovery and/or removal as the AD process converts a portion of organic nitrogen

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to inorganic ammonia, thereby increasing total ammonia nitrogen (TAN) concentration in the wastewater.

Ammonia removal can be accomplished biologically by converting ammonium into non-reactive nitrogen gas through nitrification/denitrification [4–7] or anaerobic ammonium oxidation (Anammox) [8]. Ammonia recovery processes, which allow for production of potential agricultural fertilizers, include ammonia stripping-absorption [9–13], struvite precipitation [14,15], and membrane (gas permeable and reverse osmosis (RO)) separation [16,17].

Biological nitrification and denitrification processes are unlikely as a cost-effective choice, as there are not enough bio-available organic materials in digested manure. The process also requires large reactors and energy inputs [4–7]. From a sustainability and economics perspective, the nitrogen is lost in the process to the air in non-reactive form, producing no saleable co-products [3]. Crystalline struvite in the form of magnesium ammonium phosphate is an attractive slow-release fertilizer but with limited nitrogen content. However, because of the low amounts of magnesium relative to ammonia concentrations, inputs of magnesium reagent are often required for the treatment of digester effluent, which can result in an expensive process [18]. Moreover, the majority of phosphorus in anaerobically digested effluent is tied up in a fine suspended calcium-phosphate solid, thus becoming unavailable for struvite formation [19]. Membrane processes, while useful in obtaining greater levels of wastewater purification, require costly chemical pH treatment, either through prior acidification when utilizing RO or alkaline insertion for fast transportation of free ammonia through gas-permeable membranes [16,17]. In addition, membranes might require extensive pre-treatment of the manure wastewaters, which are typically high in suspended solids content, while also being prone to high energy and operational and maintenance inputs [20].

Ammonia stripping is a potentially applicable process as there is a considerable concentration of ammonia in the effluent due to the biological conversion process of AD. A saleable ammonium salt fertilizer product can be produced from subsequent absorption of the stripped ammonia with an acid [9]. Unfortunately, from a cost perspective, traditional ammonia air stripping requires either addition of alkali chemical to elevate the pH or heat to increase the temperature to release the free ammonia [9,21,22]. Additionally, traditional stripping tower systems utilizing packing media or tray towers are prone to solids interception as the dairy AD effluent often contain high contents of solids [2].

A challenge that needs to be overcome in order to raise the pH is the high buffer capacity of digested effluent due to the presence of significant bicarbonate/carbonate, phosphate, and ammonia buffers, with total alkalinity (TA) of digested effluent being elevated by 50–60% [2]. Dissolved inorganic carbon (DIC), TAN, TA and pH are interrelated to the concentration and transformation of supersaturated CO_2 produced during AD with dissolved carbonate, bicarbonate, ionized ammonium and free ammonia mutually related within complex equilibriums. Appreciable levels of calcium, magnesium and phosphorus in effluent from dairy manure digestion also contribute to a high alkalinity [15,19] and these intricate relationships. Detection of concentrations of each species is difficult, requiring chemical equilibrium modeling from a few simple input species for prediction of the rest of the other chemical species.

The hypothesis for this paper is that a sufficient pH could be achieved allowing for ammonia to be efficiently recovered without alkali chemical input, requiring only air-stripping, elevated temperature supplied by recovered waste heat, and without use of a complicated stripping tower. A laboratory study was conducted to verify the feasibility of this strategy by investigating several limiting factors including temperature, bubble size, liquid depth and air flow rate. A chemical species modeling effort was completed and the chemistry behind aeration was elaborated through model for optimized recovery of ammonia from dairy AD effluent.

2. Materials and methods

2.1. Anaerobic digested manure

Anaerobic digested manure was collected from a commercial dairy digester in Lynden, WA. The digester was operated under mesophilic condition (38 °C) with a hydraulic retention time (HRT) of 22 days. The digester effluent was screened through a 0.5 mm screen to remove coarse fiber before the experiments. The detailed physical/chemical characteristics of the undigested and digested manure are listed in Table 1.

2.2. Experimental setup and operation

2.2.1. Effect of temperature on ammonia stripping

Experiments were conducted in a 500 ml Pyrex bottle with a working volume of 400 ml. The aeration bottle was placed in a water bath with auto-controlled temperature (ISOTEMP 1013D, Fisher Scientific, Pittsburg, PA). The temperature was set to 35, 55, and 70 °C, respectively for different tests. Air was pumped into the bottom of the bottle, through an air stone (Aqua-Mist, Hauppauge, NY) by a peristaltic pump (Masterflex L/S 7524-40, Fisher Scientific, Pittsburg, PA) at a constant flow rate of 400 ml/min. Before the aeration started, AD effluent was preheated for one hour to obtain the desired temperature. Outlet gas samples were taken with a 35 ml syringe and stored in 12 ml vacuumed borosilicate vials (Exetainer, Labco Limited, Wycombe, England). Ten ml of liquid sample was taken each time with a 5 ml pipette.

2.2.2. Effect of bubble size, liquid depth and air flow rate on ammonia stripping

Experiments were conducted in two 5-gallon column reactors containing either a coarse bubble diffuser (EPDM flex cap diffuser, Mooers Products Inc., Milwaukee, WI) or a micro-bubble diffuser (SSI-AFD270 (9″)-EPDM Membrane Disc, Stamford Scientific International, Inc., Poughkeepsie, NY) installed at the bottom of the reactor. The reactor chamber was temperature controlled at 40 ± 2 °C. Air was pumped to the reactor through a blower (Sweetwater S-41, Aquatic Eco-Systems Inc., Apopka, FL) and the flow rate was controlled by a flow meter (GF-6451–1250, Gilmont Instruments, Barrington, IL). Three liquid depths (2, 5, and 10 cm) and four air flow rates (5, 10, 20, and 35 LPM (l/min)) were tested with sampling procedures following those described in Section 2.2.1.

Table 1
Properties of the raw dairy manure and digested dairy manure.

	TAN (mg/L)	DIC (mg/L)	Alkalinity (mg$CaCO_3$/L)	pH	Dissolved CO_2 (mL/L)[a]
Dairy manure	1.760 ± 95	984 ± 27	8.960 ± 460	6.95 ± 0.14	527 ± 104
Digested dairy manure	1.443 ± 27	845 ± 10	14.230 ± 853	7.80 ± 0.19	846 ± 121

[a] Tested from the collected gas by applying vacuum of 27 in Hg for 2 h at 55°C.