Journal of Environmental Management 176 (2016) 1–10

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process

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A R T I C L E I N F O

Article history:
Received 17 December 2015
Received in revised form
3 March 2016
Accepted 4 March 2016
Available online 29 March 2016

Keywords:
Ammonia stripping
Chemical treatment
Dewaterability
Manure digestate
Turbulent mixing
Total solid

A B S T R A C T

In this study, ammonia stripping by means of a turbulent mixing process followed by pH neutralization was investigated as a simple and cost-effective ammonia removal technique to treat raw manure digestate. Batch tests conducted using CaO, NaOH and H_2O_2 to control pH and temperature and combinations thereof showed that sodium hydroxide was the most suitable chemical, as it is easy to handle, minimizes treatment time and costs, does not increase the solid content of the sludge and allows to easily control the stripping process. NaOH dosage mainly depended on buffering capacity rather than on total solid content. The analysis of the ammonia stripping process indicated that ammonia removal was strongly dependent on pH, and ammonia removal rate followed the pseudo-first-order kinetics. Total solid content slightly influenced TAN removal efficiency. When NaOH was applied to treat raw digestate at pH 10 and mean temperature of 23 ± 2 °C, TAN removal efficiency reached 88.7% after 24 h of turbulent mixing stripping, without reaching inhibitory salinity levels. Moreover, pH neutralization with sulfuric acid following the stripping process improved raw digestate dewaterability.

1. Introduction

In past two decades, livestock production has grown rapidly, particularly in the developing world (FAOSTAT, 2013). Manure may be used as a fertilizer in agriculture according to specific nutrient requirements of the crops. Nevertheless, great manure production may increase global warming caused by the emission of greenhouse gases (GHG) (Smith et al., 2009), aquatic eutrophication caused by the leaching of phosphorus (P) and nitrogen (N) compounds into underground and surface water bodies (Smith et al., 1998), and soil acidification due to the release of gaseous ammonia (NH_3) (Sandars et al., 2003). In order to avoid negative impacts on the environment and still be able to exploit the potential of manure to be used as a powerful fertilizer, the development of combined treatments of manure is needed, especially in contexts of nutrient surplus, where the European Nitrates Directive 91/676/EEC limits soil application rates of manure to a maximum of 170 kg N ha^{-1} yr^{-1} in terms of total N (nitrate-vulnerable zones).

Anaerobic digestion (AD) of livestock manure has been widely applied in the last years, because of the capacity of this treatment to stabilize manure, minimize sludge, reduce GHG and produce energy (Appels et al., 2011). AD does not affect N content of the treated substrate even if it favors the mineralization of organic N. Thus, AD produces an anaerobic digester liquid effluent, the so called raw digestate, characterized by a total solid content of 50–60 gTS L^{-1}, rich in N, mainly in form of ammonium (NH_4^+), and relatively poor of readily biodegradable organic matter.

Usually, post-treatment by means of a solid-liquid separation unit is recommended for better managing the land application of the digestate. Solid-liquid separation provides two material fractions that can be independently handled. The solid fraction (about 20–25% TS) can be used as soil amendment, or undergo further processing (e.g. composting, drying, etc.) to produce added value products. The liquid fraction, called digester supernatant, is rich in total ammonium nitrogen (TAN) and relatively poor in organic carbon. It can be used to irrigate the fields in the livestock surroundings. Alternatively, it may be subjected to post-treatment so as to remove or recover nitrogen. When the cropland is not sufficient for the disposal of excess N, decreasing TAN content both in raw digestate and digester supernatant is a major challenge. In this context, identifying the most efficient and low-cost process for nitrogen reduction is essential.

TAN content may be reduced by means of biological, chemical or

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http://dx.doi.org/10.1016/j.jenvman.2016.03.007
0301-4797/

physical processes (Magrí et al., 2013). Biological processes are classified as removal techniques, as they convert ammonium into dinitrogen gas, which is released into the atmosphere. Biological processes are usually applied to digester supernatants rather than raw digestate, in order to prevent the build-up of solids and any problems linked to microbial activity. The ratio of chemical oxygen demand (COD) to TAN of digester supernatants is usually low; therefore, traditional nitrification and denitrification is an expensive process owing to high costs for both oxygen supply and external carbon source addition (Scaglione et al., 2013). The innovative autotrophic nitrogen removal (ANR) process, partial-nitritation/anammox, has been successfully applied to treat digester supernatants from livestock manure, achieving a N removal efficiency of 85–90% and simultaneously reducing sludge production and energy consumption (Fux and Siegrist, 2004; Scaglione et al., 2015). On the other hand, ANR processes require careful control and automation that may involve high investment costs.

Thermal drying is a thermal-physical treatment, which has been applied to both raw digestate and solid fraction in order to reduce the amount of water while recovering nutrients (Rehl and Müller, 2011). TAN is almost entirely released into the air during the drying processes (Maurer and Müller, 2012) and can be recovered from the gas-phase. However, the process needs a very high amount of energy (European Biogas Association, 2013).

The efficacy of chemical and chemical–physical processes depends on the type and amount of the chemicals used. Escudero et al. (2015) achieved ammonia removal efficiencies of 95% and 97% by treating raw digestate and digester supernatant with struvite precipitation, respectively. However, this recovery technique has inherent limitations, such as high cost of reagents and the need to strictly control the pH (Pastor et al., 2010). Another technique for recovering nutrients is the ammonia stripping process in combination with absorption for the production of ammonium sulfate. Digestate characteristics, in terms of basic pH, high ammonia concentrations and high temperature, make ammonia stripping more feasible compared to other nitrogen removal techniques (Bonmatì and Flotats, 2003).

Overall, the ammonia stripping process includes four major in series operations: (1) conversion of ammonium ions (NH_4^+) to ammonia gas (NH_3) (ammonia dissociation equilibrium), (2) diffusion of NH_3 to the air-water interface (water-side mass transfer), (3) release of NH_3 to the air at the interface (volatilization), and (4) diffusion of NH_3 from the air-water interface into the air above (air-side mass transfer). The whole process depends on pH, temperature and mass transfer area. Air, steam or biogas is used to separate the gaseous NH_3 from the liquid phase. Strippers can be operated continuously or in a batch mode. NH_3 is thereafter absorbed in an acid solution in order to produce a value-added fertilizer (a 40%–60% ammonium sulfate solution), with low organic contamination (Laureni et al., 2013). The effluent of the ammonia stripping process can be used in agriculture after pH neutralization, usually obtained by applying sulfuric acid (H_2SO_4).

A significant issue is the design of the contacting system between contaminated water and the gas used to strip out the NH_3. The goal is to maximize the extent of contact (maximum rate of mixing, highest specific surface area) while minimizing energy costs associated with the equipment design. The most common mass transfer design for air stripping systems uses continuously packed towers (Srinath and Loehr, 1974). The process is typically conducted at temperatures higher than 20 °C and pH above 9. The air to liquid ratio of the flow also significantly affects the performance of the process. High N removal efficiency (approximately 93%) was reached in a packed tower by working on a digester supernatant at pH 10.5, temperature of 50 °C and elevated air consumption ($Q_G/V_L = 1.18$ L s^{-1} L^{-1}) (Guštin and Marinšek-Logar, 2011). Recently, a stripping tower has been also applied to raw digestate characterized by organic matter content below 10 g COD L^{-1} and total solid content below 12 g TS L^{-1}, under constant temperature (50 °C) and constant air consumption (0.12 L s^{-1} L^{-1}) (Laureni et al., 2013). Ammonia stripping efficiencies above 80% and 95% were reached at pH 8.5 and 9.5, respectively. However, when effluents with high COD and TS contents (70–80 g COD L^{-1} and 50–52 g TS L^{-1}, respectively) were tested, TAN removal efficiencies were below 70%. In full-scale application, packed towers are not suitable for air stripping of manure digestate, because they lead to scaling problems and the fouling of packing media.

Other options include spray towers, low profile units, bubble diffusers, aspirators, surface aerators, and high intensity mixers. Recently, new gas–liquid contactors have been designed, such as the semi-batch jet loop reactor (Değermenci et al., 2012) and the water-sparged aerocyclone reactor (Quan et al., 2009). Selection of the appropriate technology is often site-specific. To the best of our knowledge, a simple and economic technology to be applied in the agricultural context is needed. The use of mixers that guarantee adequate turbulent mixing thus ensuring the transfer of ammonia from the liquid to the gas phase without problems related to the presence of solids, appears to be a simple technique to directly treat the raw digestate, enabling reduction of both investment costs and management problems in the perspective of industrial implementation of the process.

However, ammonia stripping from raw manure digestate by means of turbulent mixing has never been specifically studied in detail, therefore several aspects of the process remain to be clarified.

The major aim of the present study was to optimize ammonia stripping from manure digestate in order to propose a suitable technology to be applied in the agricultural context, thus improving digestate management. As a first step, optimal type and dosage of chemicals for pH and temperature control in the stripping process were systematically determined based on pH and T adjustments. Then, the effects of TS content and buffer capacity on dosage of chemicals were studied. Ammonia stripping kinetic was studied at the operative conditions that resulted to be optimal from previous batch tests. Finally, we investigated the capacity of the studied ammonia stripping and neutralization processes to enhance dewaterability of the anaerobic sludge.

2. Materials and methods

2.1. Anaerobic digestate and chemicals

The raw digestate was sampled from a large-scale anaerobic digester plant (Sant'Anna d'Alfaedo, Italy), which was fed with cow manure (29.0%), cow slurry (29.7%), pig slurry (29.7%) and poultry manure (11.6%). All samples were stored at 4 °C for a period up to than 3 weeks, in order to prevent reduction of organic matter and ammonia nitrogen content (Laureni et al., 2013). Raw digestate pH ranged between 8.4 and 8.6, 58.75 ± 1.5 gTS L^{-1}, TAN concentration in the range of 4000 and 5000 mgN L^{-1}, soluble COD content of 13,880 ± 2560 mgCOD L^{-1} and 5 gNa^{+} kgTS^{-1}.

The chemicals tested in the ammonia stripping process were: calcium oxide (92% minimum on weight, CaO), 19.1 M sodium hydroxide (NaOH) solution and hydrogen peroxide (39% W/V, H_2O_2). The pH neutralization was performed by adding 98% sulfuric acid