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Enhancement of microbial density and methane production in advanced anaerobic digestion of secondary sewage sludge by continuous removal of ammonia

Bing Tao [a], Joanne Donnelly [a], Ivo Oliveira [a], Ruth Anthony [a,b], Victoria Wilson [b], Sandra R. Esteves [a,*]

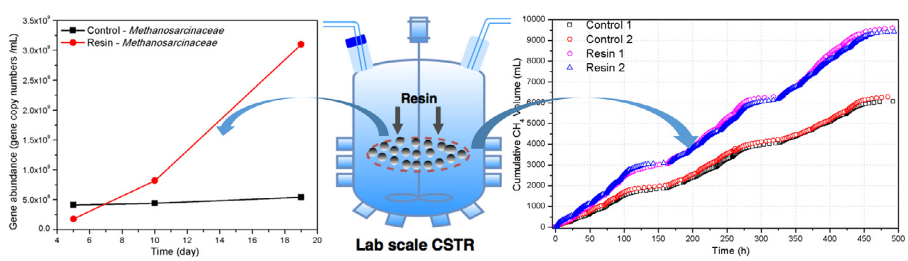
[a] *Wales Centre of Excellence for Anaerobic Digestion, Sustainable Environment Research Centre, Faculty of Computing, Engineering and Science, University of South Wales, Pontypridd CF37 1DL, UK*

[b] *Welsh Water, Nelson, Treharris CF46 6LY, UK*

HIGHLIGHTS

- NH_3 inhibition was mitigated by continuous NH_4^+ removal using ion-exchangers.
- CH_4 yields improved by 54% when NH_3 reduced from 630 to 92 mg/L.
- Population density of *MSC* and *MBT* increased by over 6 and 5 times.
- Total bacterial density increased by over 2 times facilitated by ammonia reduction.
- Enhanced carbohydrates and proteins hydrolysis was achieved with ammonia removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia inhibition mitigation in anaerobic digestion of high solids content of thermally hydrolysed secondary sewage sludge by the NH_4^+ affinitive clinoptilolite and a strong acid type ion-exchange resin S957 was investigated. Continuous NH_4^+-N removal was achieved through ion-exchanging at both temperatures with average removals of 50 and 70% for the clinoptilolite and resin dosed reactors, respectively. Approximate 0.2–0.5 unit of pH reduction was also observed in the dosed reactors. The synergy of NH_4^+-N removal and pH reduction exponentially decreased free NH_3 concentration, from 600 to 90 mg/L at 43 °C, which mitigated ammonia inhibition and improved methane yields by approximately 54%. Microbial community profiling suggested that facilitated by ammonia removal, the improvement in methane production was mainly achieved through the doubling in bacterial density and a 6-fold increase in population of the *Methanosarcinaceae* family, which in turn improved the degradation of residual volatile fatty acids, proteins and carbohydrates.

1. Introduction

Anaerobic digestion (AD) is a well-established process for sewage sludge treatment in Europe and it is estimated that 66% of sewage sludge is treated via AD in the UK and 90% in Germany (European Biogas Association, 2014). As secondary sewage sludge is particularly difficult to treat, a number of pre-treatment processes have been investigated and thermal hydrolysis is currently being implemented on over 55 full scale plants across the world and deployment continues to grow.

* Corresponding author.
E-mail address: sandra.esteves@southwales.ac.uk (S.R. Esteves).

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Despite the attractive benefits offered by AD, a number of digesters have often suffered inhibition imposed by compounds, among which ammonia is the most common one. It has been proposed that ammonia inhibits AD mainly through changing intracellular pH of methanogens, increasing maintenance energy requirements and suppressing a specific enzyme reaction (Chen et al., 2008; Rajagopal et al., 2013), although knowledge of how ammonia toxicity occurs is still limited. Free ammonia nitrogen (FAN, NH_3) is the main cause of inhibition as it can freely permeate cell membranes. It is recognized that when total ammonia nitrogen (TAN, i.e.·NH_3-N + NH_4^+-N) exceeds 3000 mg/L (McCarthy, 1964), the AD process is inhibited at any operating pH and severe methanogenesis inhibition occurs when TAN exceeds 4000 mg/L (Procházka et al., 2012).

Typically, to counteract ammonia inhibition, anaerobic digesters have been operated using co-digestion substrates with high carbon content or using water for dilution. Alternatively, digesters have been operated sub-optimally at lower loading rates and reduced conversions with a high level of volatile fatty acids (VFAs) accumulation (Banks et al., 2011) facilitated by a high buffering from the level of ammonium. Other researchers on the contrary have identified that after adaptation of the microbial community to high levels of ammonia, biogas production can, however, occur without instability or reduced performance (Kovács et al., 2015) and particularly, *Methanosarcina sp.* have been reviewed as highly tolerant to high ammonia levels (De Vrieze et al., 2012). Ammonia impact on digestion is therefore a topic of argument among the academic and industrial communities.

Some research on ammonia removal aiming to reduce inhibition or recover the nutrient has also been conducted. There are a number of reports applying different methods to remove/recover ammonia from anaerobic digesters. Ammonia stripping requires increasing pH of effluent to 10–11 with addition of alkali and also demands heat and/or constant gas flow to effectively remove ammonia (Oliveira et al., 2013; Park and Kim, 2015; Tao and Ukwuani, 2015), hence, it is normally operated in batch mode using anaerobic digestate instead of using an online ammonia removal method. Similarly, struvite precipitation requires adjustment of pH and addition of chemicals, and therefore it has been used offline as well (Cerrillo et al., 2015; Romero-Güiza et al., 2015). With recent advancements in membrane technology, counteracting ammonia inhibition has been investigated using both pressure- and electrical-driven membrane technologies. Lauterböck and colleagues reported that continuous removal of ammonia, which resulted in a drop of pH and VFA levels, has led to a higher gas production (Lauterböck et al., 2012, 2014), however microbial communities and detailed degradation rates were not investigated. Desloover and co-workers investigated the feasibility of applying electrical-driven cation exchange membrane to extract ammonia from the effluent of an upflow anaerobic sludge blanket reactor fed by diluted molasses solution (Desloover et al., 2012, 2015). The simultaneous ammonium extraction and pH control achieved by the electrochemical unit improved the methane production by 4.5 times in comparison to the control reactor. Despite the advantages, the membrane unit suffered fouling from suspended solids and that is why most studies involving membranes focused on the treatment of either a model solution or low suspend solids wastewater effluents only (Desloover et al., 2015; Lauterböck et al., 2012).

Ammonium removal by ion-exchange has been reported by many researchers. Natural zeolites have also been used to mitigate ammonia inhibition of AD (Wang et al., 2011; Zheng et al., 2015). The adsorption of ammonium ion by natural zeolites has shown improved stability of digesters and better methane production (Ho and Ho, 2012; Zheng et al., 2015). However, the ion-exchanging capacities of zeolites are usually quite low, which leads to the need for quite high zeolite dosage. For example, it has been demonstrated that the methane production was improved by only 26% at a dosage of 10 g/L, while it was improved by 60% when dosage was increased to 20 g/L (Ho and Ho, 2012). Also, natural zeolite mostly exchanges non-proton cations (e.g. Ca^{2+}, Mg^{2+}) for ammonium ion; thus, there is usually little effect in pH reduction by natural zeolites. To the authors' knowledge, there is little information available on how the microbial community is affected during the ammonium removal by ion-exchanging materials. Therefore, in this work, continuous ammonium removal using ion-exchanging materials was investigated, with the objective of understanding how simultaneous ammonium removal and pH reduction impact on the performance of digesters and especially the microbial community characteristics.

2. Materials and methods

2.1. Ion-exchanging materials

Two ion-exchanging materials, including clinoptilolite and a strong acid type ion-exchange resin S957, were evaluated for ammonium removal. Clinoptilolite with particle size of 1–2 mm was obtained from Rota Mining Corporation, Turkey. The Sulfonic and phosphonic acid functionalized cation exchange resin S957 was provided by Purolit® (Llantrisant, UK). Zeolite refers to clinoptilolite and resin refers to S957 in this work, when no other specification is given. The typical characteristics of the used zeolite and resin are summarized in Table 1.

2.2. Setup of the anaerobic digesters

Twelve lab scale continuously stirred-tank reactors (CSTR) (1 L size) were set up and operated at 37 and 43 °C (6 reactors on each temperature). The reactor configurations comprised of 3 types: control, zeolite and resin dosed reactors. Each reactor condition was run in duplicate. The temperatures were selected to simulate the full scale mesophilic advanced anaerobic digesters at Cardiff wastewater treatment works (WWTWs) treating thermally hydrolysed secondary sewage sludge with an incoming feed of 8–9% total solids (TS). As sludges are pre-treated at 165 °C and 6 bar, during hot weather conditions and due to sub-optimal heat exchanger performance, the actual temperature of the digesters are at the higher end of mesophilic temperatures (42–43 °C), hence 43 °C was selected as well.

Inoculum for seeding the reactors were obtained from the full scale advanced anaerobic digesters from Cardiff WWTWs (Cardiff, UK). The laboratory reactors were fed with thermally hydrolysed waste activated sludge (THWAS) sourced from Cardiff WWTW. Typical characteristics of THWAS is summarized in Table 2. Each reactor was initially seeded with 800 g of digestate inoculum, heated to 37 or 43 °C and then fed with thermally hydrolysed sludge and allowed to acclimatise for 14 days to allow for a similar

Table 1
Summary of the characteristics of the used zeolite and resin.

	Clinoptilolite	Resin S957
Structure	Monoclinic platy crystals	Polystyrene cross-linked divinylbenzene
Ionic form	Ca^{2+}, Mg^{2+}, K^+, Na^+	H^+
Physical appearance	Angular granules	Spherical beads
Particle size (μm)	1000–2000	425–825
Pore size type	Microporous	Macroporous
Water content	<3%	45–55%
Acidic capacity (mmol/g)	1.5–1.8	11.25