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High pH buffer capacity biomass fly ash-based geopolymer spheres to boost methane yield in anaerobic digestion

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A B S T R A C T

Anaerobic digestion (AD) is a well-known technology for organic waste treatment with recognised environmental benefits including the generation of renewable energy (methane) and other added-value products. However, when applied to very easily biodegradable substrates, there is a need to mitigate the sudden pH drop, in order to improve the stability and feasibility of the process. In this work, and for the first time, waste-based geopolymer spheres were used as pH regulators in AD. The influence of the binder composition and content on the ability to control pH and on the methane yield was evaluated. The pH buffer capacity of the geopolymers can be controlled by the fly ash content in the composition, with higher contents leading to higher alkalis leaching and narrower pH fluctuation over time. The spheres promoted an excellent control of pH in batch operated anaerobic reactors (up to 70 days), which increases the stability and efficiency of the systems. The pH range in the reactor without spheres remained mostly between 3.84 and 4.38, preventing methane production, whereas in reactors with spheres pH was mostly kept between 6.45 and 7.94. The fast pH stabilization during the entire experiments, which occurred with fly ash-based geopolymers, stimulated the early methane production, demonstrating the huge potential of these innovative spheres as a pH buffering material. Using this innovative waste-based material, instead of commercial alkaline materials, enhances process simplicity (prevent the need for continuous pH adjustment) and sustainability, which may overcome the limitations associated with the existing applications such as the use of substrates with a high acidogenic potential and, therefore, contribute to the spread of AD technology.

1. Introduction

Energy production from renewable sources is expected to reach 20% of the European Union (EU) total energy needs by 2020 (Directive EC, 2009), while even more demanding targets have been recently proposed by the Commission (27% by 2030) (Proposal for a Directive, 2016). The latter exerts tremendous pressure on EU countries to change their energy supply from fossil fuels to cleaner and more efficient technologies. Biogas has been emerging as energy source that can lessen the greenhouse gases emissions in comparison with traditional fossil fuels, and can be accessed on demand, unlike other more intermittent renewables (e.g. wind and solar) (Whiting and Azapagic, 2014). Biogas can be produced by anaerobic digestion (AD) of organic substrates through a complex process involving hydrolysis, acidogenesis, acetogenesis and methanogenesis reactions (Zhang et al., 2016). In AD the main products are methane and carbon dioxide, while other gaseous compounds such as hydrogen and nitrogen are generated in lower amounts (Kamali et al., 2016). The process efficiency is strongly affected by operational and environmental conditions such as temperature (Liu et al., 2016), pH (Latif et al., 2017), volatile fatty acids (VFAs) (Rico et al., 2015), among others (Zhang et al., 2014a). In fact, the AD process, and methanogenesis in particular, are very sensitive to pH fluctuations in the system. Anaerobic bacteria require distinct pH for their growth, ranging from 4.0 to 8.5 for fermentative microorganisms and between 6.5 and 7.2 for the more

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sensitive methanogens (Zhang et al., 2014a). Maintaining a narrow pH range in AD is challenging when using substrates with high organic loads due to rapid acidification, which hinders the methanogenesis (Saddoud et al., 2007). To overcome the expected drop in systems efficiency two approaches are commonly used: i) alkaline pre-treatment of the wastes (Dai et al., 2016); or ii) adding commercial alkaline materials (e.g. sodium hydroxide (NaOH) or calcium carbonate ($CaCO_3$)) to the AD reactor. Recently, an innovative and greener alternative was reported, which was the use of waste-containing geopolymer monoliths (Novais et al., 2016a) or spheres (Novais et al., 2017) that acted as pH regulators. When immersed in water, these materials leached significant amounts of OH^- from their structure, thus providing prolonged pH adjustment. Other investigations have shown that the alkalis leaching from the geopolymers can be controlled by the activator concentration (Zhang et al., 2014b), nature of the binder (Novais et al., 2017), solid-to-liquid ratio (Bumanis and Bajare, 2014) and geopolymers' porosity (Novais et al., 2016a). The latter suggests the possibility of using geopolymers as pH buffering materials in AD. However, despite the promising results in water medium, the use of geopolymers in AD systems is rare. Rugele et al. (2015) reported the use of an alkaline composite material (cubic specimens) in AD. These authors observed a 22% increase in the biochemical methane potential in comparison with reactors without the composite material. These findings demonstrate the potential of using geopolymers, instead of commercial alkaline materials, to increase the efficiency and stability of the digestion process. Nevertheless, additional studies are required to fully understand the influence of geopolymer composition and content on the pH in AD.

In this research work biomass fly ash-based geopolymer spheres were used to control the pH in anaerobic digesters. The use of waste-based geopolymeric spheres with high buffer capacity could be an effective solution, in comparison with commercial alkaline materials, to promote prolonged pH control in the AD of highly biodegradable waste streams. It is recognised that the methanogenic digestion of these substrates is problematic. The proposed strategy may enhance systems stability and efficiency (e.g. methane yield) and simplicity (prevent the need for continuous pH adjustment). This is the first ever report considering the use of geopolymer spheres and formulations made from biomass fly ash (FA) waste as pH buffering materials in AD. The influence of the binder composition (metakaolin (MK)-based or FA-based) and content on the ability to control pH in the AD of cheese whey (substrate with high acidogenic potential) was evaluated. The effective pH control (up to 70 days) achieved in the batch operated anaerobic digesters containing geopolymer spheres promoted a high methane yield, which demonstrates the significant potential of this innovative material to increase the efficiency and stability of the AD process.

2. Experimental conditions

2.1. Materials

MK (Argical™ M1200S; Univar) and FA from biomass combustion, thereafter referred as biomass FA, were used as geopolymerization precursors. The *as-received* FA contains a very broad particle size distribution which would hinder the geopolymer slurry injection to produce the geopolymer spheres. For that reason prior to mixing, the FA particles were sieved and then only the fraction with particle size below 63 μm were used.

Two alkaline activators were used: i) industrial grade sodium silicate solution (Chem-Lab, Belgium) with a $SiO_2/Na_2O = 3.09$; and ii) NaOH (ACS reagent, 97%; Sigma Aldrich). Sodium dodecyl sulfate and polyethylene glycol (PEG-600) were supplied by Sigma Aldrich.

Cheese whey powder, an industrial by-product, was selected as substrate due to its high acidogenic potential, in order to evaluate the porous geopolymer spheres' ability to control the pH in the AD process. Cheese whey was collected from a medium-scale cheese factory. A concentrated solution was prepared, and the volume of substrate to be used was determined in order to achieve an initial substrate concentration corresponding to a soluble chemical oxygen demand (COD) of 8 g/L in each bioreactor, based on previous anaerobic tests with cheese whey as substrate (Silva et al., 2013).

2.2. Geopolymers preparation

The porous geopolymer spheres were produced following a previously described procedure (Novais et al., 2017). Two compositions were prepared in which MK was partially (33 and 75 wt%) substituted by FA. These compositions were selected considering the spheres distinct leaching behaviour in water medium (Novais et al., 2017), aiming to evaluate the influence of the binder composition on the pH control in AD.

The alkaline activator was prepared in advance by adding 13.22 g of NaOH to 100.00 g of sodium silicate solution. Afterwards, the mixture of the alkaline solution, distilled water, MK and FA (amount depending on the composition) was carried out in a planetary mixer. After that, the foaming agent, sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$), was added to the blend, and mixed to obtain foamed slurry. Details of the mixture composition are presented in Table 1.

Finally the slurry was injected into a polyethylene glycol ($H(OCH_2CH_2)_nOH$) medium (under a bath temperature of 85 ± 5 °C) to produce geopolymeric spheres. The spheres were then collected and cured in controlled conditions (40 °C and 65% relative humidity) using a climatic chamber for 24 h. Afterwards, the spheres were cured at room temperature and then used in the AD batch experiments.

2.3. Anaerobic digestion batch experiments

To study the influence of geopolymer composition and dosage on the pH fluctuation in the AD process of cheese whey, two different experimental set-ups were used. All the assays were performed at controlled mesophilic temperature (37 ± 1 °C). In the first study, eight anaerobic batch assays plus one blank assay were run in duplicate in 280 mL glass vessels (250 mL working volume) for 21 days. The blank assay was performed without the addition of alkaline chemicals or spheres, while a buffer solution of $NaHCO_3$ and $KHCO_3$ was used to promote pH autoregulation in two other anaerobic batch assays, to achieve 2 and 4 g/L of alkalinity measured as $CaCO_3$. In the other six assays, geopolymer spheres (MK-based or FA-based spheres) were added in distinct amounts (20, 40 and 80 g/L) to evaluate the influence of the binder characteristics (MK-based or FA-based) and amount on the pH evolution of the AD system. In this first experimental set-up only the pH values were monitored during time. This preliminary pH evaluation was used to select the optimal formulation for studying the methane production in larger assays (1 L working capacity). In these, three anaerobic batch operated assays using cheese whey as

Table 1
Geopolymer preparation: mixture composition.

Sample name	FA content (wt.%)	Mixture proportion (g)				
		FA	MK	Alkaline activator	H_2O	Foaming agent
MK-based	33	5.00	10.00	24.38	4.15	0.59
FA-based	75	11.25	3.75			