Chemical Engineering Journal 260 (2015) 791–800

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Effect of high orthophosphate concentration on mesophilic anaerobic sludge digestion and its modeling

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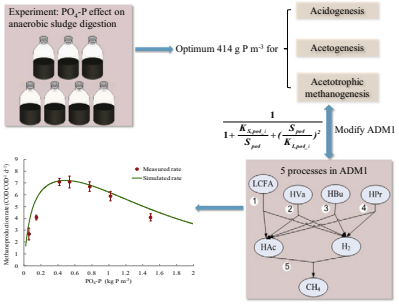
HIGHLIGHTS

- Orthophosphate affects methanogenesis, acetogenesis and acidogenesis.
- Haldane kinetics of orthophosphate inhibition is proposed for inclusion in ADM1.
- Parameters of the new model are estimated from an extensive data set.
- The new model fits the measured data well and is validated on independent data.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 11 September 2014
Accepted 15 September 2014
Available online 22 September 2014

Keywords:
Acetate inhibition
ADM1
Enhanced biological phosphorus removal
Haldane kinetics
Mesophilic anaerobic digestion
Orthophosphate inhibition

ABSTRACT

To gain insight regarding the orthophosphate influence on fatty acid dynamics and methane production during mesophilic anaerobic sludge digestion, batch experiments were conducted. The results showed that an orthophosphate concentration of 414 g P m^{-3} accelerated acetotrophic methanogenesis, acetogenesis and acidogenesis. Lower or higher concentrations slowed these processes down. Three modifications of the Anaerobic Digestion Model No. 1 (ADM1) were compared by simultaneously fitting them to a multi-experiment (7 batches), multi-variable (6 measured variables) data set. A modified ADM1 model including Haldane kinetics of orthophosphate inhibition gave the best description of the measured data while the model using non-competitive acetate inhibition showed the poorest results. It is notable that the multi-experiment, multi-variable data set could be fitted with a single parameter set. The model with Haldane kinetics of orthophosphate inhibition together with the proposed parameters can be considered as a first attempt to describe the observed orthophosphate inhibition of anaerobic digestion.

1. Introduction

Phosphorus removal from wastewater is important for preventing natural waters from eutrophication. Chemical or biological processes are usually used for phosphorus removal from wastewater. Many wastewater treatment plants are designed using the enhanced biological phosphorus removal (EBPR) process, which is based on biological uptake and transfer of phosphorus from the liquid phase to the sludge phase in excess of the amount that is removed by traditional aerobic activated sludge systems [1]. The amount of phosphorus incorporated in the EBPR sludge mass is increased from the normal value of 0.02 mg P mg VSS^{-1} to 0.06–0.15 mg P mg VSS^{-1} (0.05–0.10 mg P mg TSS^{-1}) [2]. The phosphorus-rich sludge subsequently needs to be treated and disposed of.

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http://dx.doi.org/10.1016/j.cej.2014.09.050
1385-8947/

The world-wide application of anaerobic digestion is rapidly growing, since anaerobic digestion has the ability to reduce the overall amount of biosolids to be disposed of by more than 40% while producing an energy-rich biogas (around 65% methane) [2,3]. It was revealed that more than 80% of the total biologically-bound phosphorus that had been removed previously during EBPR treatment was released during anaerobic digestion and up to 1500 g P m^{-3} soluble phosphorus can be observed in anaerobic digesters [4,5].

Bacteria, especially methanogenic bacteria, in anaerobic digestion are sensitive to their living conditions. Nutrients in the medium are vital to bacterial growth. One of the most important nutrients is phosphorus. It is one of the major constituents of living organisms and plays an important role in their metabolism. Therefore, it is significant to investigate whether and how bacteria are affected by such high phosphate concentrations in anaerobic digestion treating phosphorus-rich sludge. Surprisingly, few studies have been conducted on the phosphate effect on the reactions mediated by bacteria during anaerobic digestion. Rudolfs and Stahl [6] pointed out that the amount of phosphorus added exerted a retarding effect on gas production up to a certain concentration and increasing quantities of phosphorus caused greater inhibition of biological activities. A decreased rate of gas production with addition of phosphate buffer (2170, 4650, and 7130 g P m^{-3}) compared with that without additional phosphate (186 g P m^{-3}) was found by Van Den Berg et al. [7]. A study on the effect of phosphate supplementation on methane production from rice reported that a level of phosphate addition (465 g P m^{-3}) could accelerate the biogasification process [8] and addition of more than 620 g P m^{-3} of phosphate in the media inhibited methanogenesis [9]. However, the effect of phosphate on different processes of anaerobic sludge digestion including acidogenesis, acetogenesis and methanogenesis as well as the relationship of phosphate concentration and anaerobic digestion processes are still not well explored.

Anaerobic digestion models have been proposed since the end of the 1960s [10,11]. The Anaerobic Digestion Model No. 1 (ADM1) was developed as a unified base for modeling of anaerobic digestion [12]. Although some adjustments and extensions based on ADM1 have been made since then [13,14], the phosphate effect is hardly considered in anaerobic digestion models. Therefore, establishing a mathematical relationship between phosphate concentration and anaerobic digestion processes is beneficial to better understanding and optimizing the anaerobic digestion process for sludge treatment.

The objective of this study was to gain insight regarding the orthophosphate influence on biological processes during mesophilic anaerobic sludge digestion. Batch experiments were conducted to investigate the effect of orthophosphate concentrations on acidogenesis, acetogenesis and methanogenesis during the anaerobic digestion process. The obtained experimental results were used for the establishment of kinetics expressions, in the framework of the ADM1.

2. Materials and methods

2.1. Experimental set-up

Two sets of batch experiments were carried out. Experimental set A was conducted in identical serum bottles with a volume of 600 mL in a temperature controlled shaker (35 ± 1 °C). Each serum bottle contained 450 mL of digested sludge inoculum and 50 mL of synthetic sludge (starch 7 kg m^{-3}, toilet paper 10 kg m^{-3}, coffee creamer 11 kg m^{-3}, high fibre bran 12 kg m^{-3}, peptone 1 kg m^{-3}, yeast extract 3 kg m^{-3}, $NaHCO_3$ 3 kg m^{-3}) [15]. The digested sludge inoculum was obtained from a laboratory-scale anaerobic digester fed with waste activated sludge. The anaerobic sludge was washed and diluted with distilled water prior to its use so as to decrease the orthophosphate level. The characteristics of the mixed sludge are shown in Table 1. Soluble phosphorus (as Na_2HPO_4 and NaH_2PO_4) was added to make soluble PO_4-P concentrations of 144, 414, 535, 773, 1017, and 1489 g P m^{-3} (average values of the orthophosphate concentrations measured over time throughout the experiment). The bottle without addition of soluble phosphorus, in which the concentration of soluble PO_4-P was 57 g P m^{-3}, was labeled as Control-57. Samples were taken for analysis after gas was sampled, and then the pH value in each bottle was controlled at 7.0 ± 0.1 by adding KOH or HCl. Anaerobic conditions were achieved by purging with nitrogen gas for 20 s. The batch experiments were performed in triplicate, and their averages are reported.

For model validation, experimental set B with the same digested sludge inoculum and synthetic sludge was carried out. Soluble phosphorus (as Na_2HPO_4 and NaH_2PO_4) was added to make concentrations of soluble PO_4-P of 545 g P m^{-3}. The bottle without addition of soluble phosphorus, in which the concentration of soluble PO_4-P was 125 g P m^{-3}, was labeled as Control-125. The bottles were maintained in a temperature controlled shaker (35 ± 1 °C). In order to test the proposed model under non-pH-controlled conditions, pH values in both bottles were not controlled.

2.2. Analysis

Samples from the bottles were immediately filtered through a Whatmann GF/C glass microfiber filter. The filtrate was analyzed for volatile fatty acids (VFAs), SCOD, STOC, STN, PO_4-P, NH_4-N, and the filter residue was assayed for TSS and VSS. STOC and STN were determined by a TOC analyzer (TOC-V CPH; Shimadzu). Methane and VFAs were measured by gas chromatography [16]. The analyses of PO_4-P, NH_4-N, COD, TSS, and VSS were conducted according to standard methods [17].

2.3. Modeling approach

Models of the different processes were modified according to the experimental results with ADM1 as basic model, applying the same structure, nomenclature, and units [12]. Three ADM1 modifications were compared by simultaneously fitting them to measured data (Table 2). ADM1 was extended by introducing generalized Haldane equations of orthophosphate inhibition into the uptake process kinetics of acetate, propionate, butyrate, valerate, and long-chain fatty acids (LCFA) and was named M1. ADM1 modified by introducing non-competitive inhibition of acetate into the uptake process kinetics of LCFA, butyrate (valerate), and propionate was named M2, and the model with combined inhibition of orthophosphate and acetate into the same processes was named

Table 1
Characterization of the mixture of digested sludge inoculum and synthetic sludge.

Parameter	Description	Value	Unit
TSS	Total suspended solids	9270 ± 502	g m^{-3}
VSS	Volatile suspended solids	7090 ± 388	g m^{-3}
TCOD	Total chemical oxygen demand	9625 ± 629	g COD m^{-3}
SCOD	Soluble chemical oxygen demand	1350 ± 83	g COD m^{-3}
STOC	Soluble total organic carbon	615 ± 38	g C m^{-3}
STN	Soluble total nitrogen	53 ± 5	g N m^{-3}
VFAs	Volatile fatty acids	75 ± 5	g COD m^{-3}
S_{ac}	Acetate	44 ± 3	g COD m^{-3}
S_{pro}	Propionate	20 ± 1	g COD m^{-3}
S_{bu}	Butyrate	11 ± 1	g COD m^{-3}
S_{va}	Valerate	0	g COD m^{-3}
S_{NH_4}	Ammonium	18 ± 1	g N m^{-3}