Effect of High Orthophosphate Concentrations on Methane Production During Mesophilic Anaerobic Digestion

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ABSTRACT

The effect of orthophosphate concentrations on methane production during mesophilic anaerobic digestion of sludge was investigated using batch experiments. An intermediate orthophosphate concentration (414 g $P \cdot m^{-3}$) accelerated acetotrophic methanogenesis, while a further increase of the orthophosphate concentration slowed this process down. Extension of the Anaerobic Digestion Model No. 1 (ADM1) with a Haldane kinetics term for orthophosphate inhibition was proposed. This extension resulted in good fits to the experimental results.

KEYWORDS

Phosphate inhibition, Haldane kinetics, sludge treatment, methane production, mathematical modelling, enhanced biological phosphorus removal, wastewater treatment

INTRODUCTION

The application of enhanced biological phosphorus removal (EBPR) process for wastewater treatment is rapidly growing. It was reported that during anaerobic digestion more than 80% of the total biologically-bound phosphorus that has been removed previously during EBPR treatment is released to the liquid phase and up to more than 1500 g $P \cdot m^{-3}$ soluble phosphorus can be observed (Jardin and Popel, 1994). Bacteria in anaerobic digestion and especially methanogenic bacteria are sensitive to their environment. It is thus important to investigate whether and how the bacteria are affected by such high phosphate concentrations during anaerobic digestion. However, few studies have been conducted on the effect of phosphate on anaerobic digestion (Lei et al., 2010; Van den Berg et al., 1974). Besides, the phosphate effect is hardly considered in anaerobic digestion models.

The aim of this study was to investigate the orthophosphate influence on methane production during mesophilic anaerobic digestion and to establish a mathematical relationship between the orthophosphate concentration and methane producing processes.

MATERIALS AND METHODS

Batch experiments were conducted in serum bottles maintained in a temperature controlled shaker (35 ± 1 ºC). Each serum bottle contained 450ml of digested sludge inoculum and 50ml of synthetic sludge. Soluble phosphorus (as Na_2HPO_4 and NaH_2PO_4) was added to make soluble PO_4-P concentrations of 144, 414, 1017, and 1489 g $P \cdot m^{-3}$. The bottle without additional soluble phosphorus, in which the concentration of soluble PO_4-P was 57 g $P \cdot m^{-3}$, was labeled as Control57. The pH value in each bottle was controlled at 7.0 ± 0.2 by regularly adding sodium hydroxide (NaOH) or hydrochloric acid (HCl). Anaerobic conditions were achieved by purging with nitrogen gas for 20 seconds. Samples from the bottles were immediately filtered through a Whatmann GF/C glass microfiber filter. The filtrate was analyzed for VFAs and PO_4-P, the latter being measured by the vanadomolybdophosphoric acid colorimetric method (APHA, 1998). Volatile fatty acids (VFAs) and methane were measured by gas chromatography (Chen et al., 2007).

Anaerobic Digestion Model No. 1 (ADM1), applying the same structure, nomenclature, and units, was modified to include the orthophosphate effect according to the batch experiment results (Batstone et al., 2002). Modelling and simulation were done with the WEST software (Mikebydhi.com).

RESULTS

The normalized cumulative methane productions with additional orthophosphate were all higher than 1, indicating that the cumulative methane productions with additional orthophosphate were all faster than Control57 but the extent of methane production was finally independent of the orthophosphate concentration (**Fig. 1**). P414, followed by P1071, demonstrated the fastest methane production, while P1489 and P144 showed slower methane production during the first month. Such results indicated that the optimum concentration of orthophosphate for the cumulative methane production was, among the concentrations tested, 414 g P·m^{-3}; lower or higher concentrations slowed the progress down. Acetate accumulation started right away because of the hydrolysis of organic substance (**Fig. 2**). After about 6 days operation, the acetate concentration in P414 decreased sharply at the highest rate, while it decreased at the slowest rate in Control57. The acetate concentration profile for P1489 was similar to that of P144. The acetate decrease went faster with an increase of orthophosphate concentration from 57 to 414 g P·m^{-3}, and slowed down again with a further increase of the orthophosphate concentration. This trend was the same as the one of methane production (**Fig. 1**). The above results indicate that the orthophosphate concentration affects the methanogenic process mainly by the acetate uptake process, and an adequate level of orthophosphate (414 g P·m^{-3}) accelerates the acetate uptake process while a further increase of the orthophosphate concentration slowed this process down.

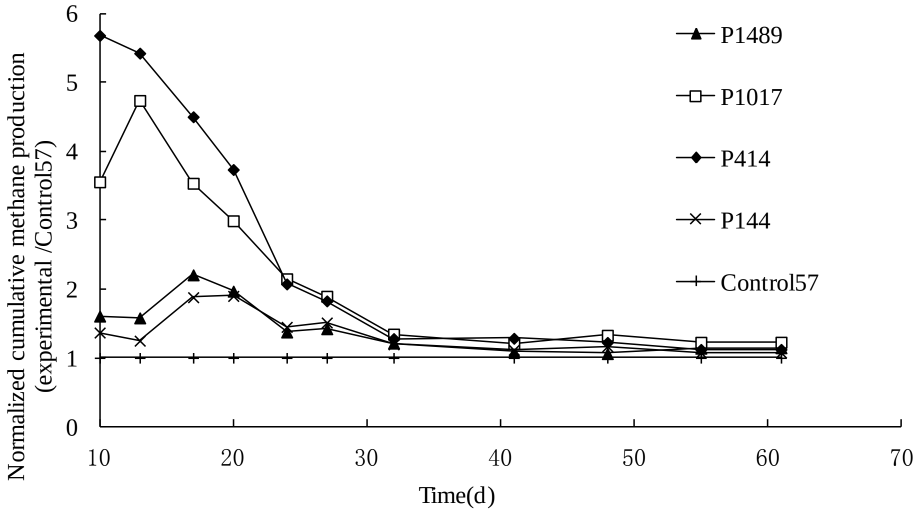

Fig. 1 Cumulative methane production (normalized with respect to Control57) from batch digesters containing different orthophosphate concentrations.

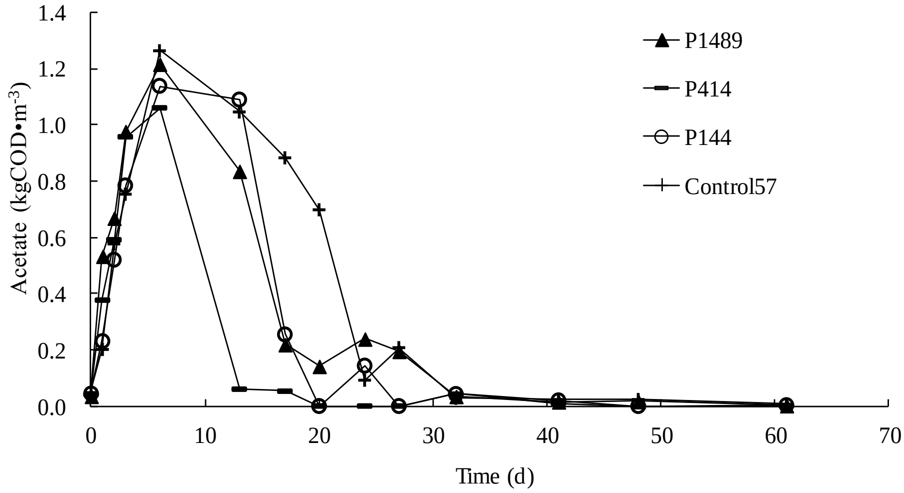

Fig. 2 Measured acetate concentration profiles at different orthophosphate concentrations.

According to the measured results, ADM1 was extended to describe the observations by introducing a Haldane equation of orthophosphate inhibition into acetate uptake process:

$$\rho = k_{m,ac}\frac{S_{ac}}{K_s + S_{ac}}\frac{\mathbf{1}}{\mathbf{1}+\frac{\boldsymbol{K_{S,po4\_ac}}}{\boldsymbol{S_{po4}}}+(\frac{\boldsymbol{S_{po4}}}{\boldsymbol{K_{I,po4\_ac}}})^2}X_{ac}I_{pH}I_{IN,\lim}I_{NH3,Xac} \quad (1)$$

To evaluate the model's performance Theil's inequality coefficient (TIC, Zhou, 1993) was used as it allows judging whether there is a significant difference between simulated and measured results. If it is less than 0.3 the model adequately describes the data. The TIC of the cumulative methane production at each orthophosphate concentration was less than 0.05, illustrating that the profiles of cumulative methane production simulated by the modified ADM1 fitted well with measured profiles in all situations (**Fig. 3**).

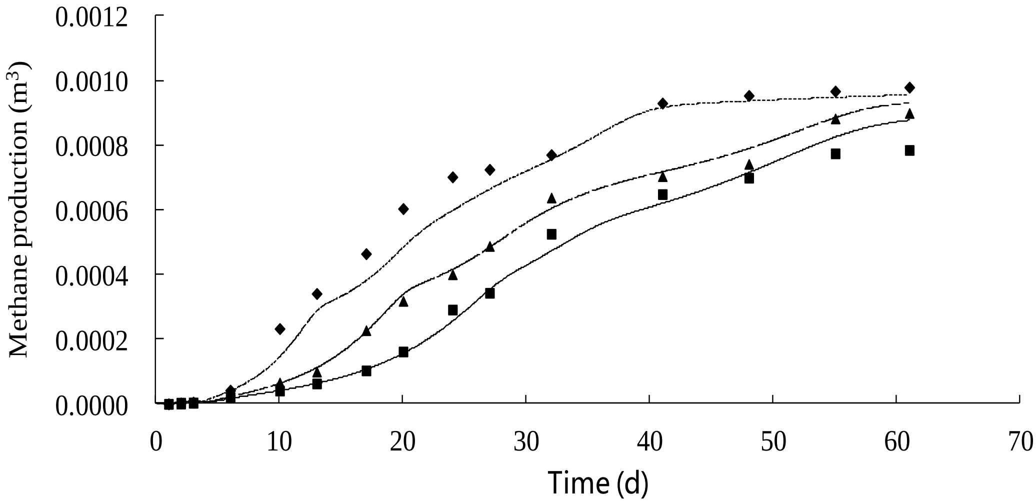

Fig. 3 Measured and simulated cumulative methane productions

■ Control57 ◆ P414 ▲ P1489

$TIC_{Control57}$=0.04 TIC_{P414}=0.05 TIC_{P1489}=0.02

CONCLUSIONS

Batch experiments indicated that an intermediate orthophosphate concentration (414 g P·m^{-3}) accelerated acetotrophic methanogenesis. Lower or higher concentrations slowed this process down. The orthophosphate effect on the acetate uptake rate was adequately described by Haldane kinetics.

No study was conducted so far to explain the orthophosphate effect on methane production. In the field of antibiotic and secondary metabolites by fermentation, several mechanisms were studied and discussed to explain the effect of phosphate (Martin, 1977). It was pointed out that negative phosphate control of antibiotic biosynthesis in *Streptomyces lividans* and *Streptomyces coelicolor* is mediated by the two-component PhoR-PhoP system (Martin, 2004). However, whether this mechanism can also explain the orthophosphate effect on anaerobic digestion needs further study given the fact that methanogens are not known to be producers of secondary metabolites.

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