Alternative approach to estimate the hydrolysis rate constant of particulate material from batch data

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HIGHLIGHTS

- An alternative to the commonly used first-order approach is presented.
- A relationship between k_h and the 1% criterion of the VDI 4630 is deduced.
- Equation is proposed to directly calculate k_h without the need for data fitting.
- Hydrolysis constant k_h can then easily be read-off from a table.

ARTICLE INFO

ABSTRACT

As anaerobic batch tests are easy to conduct, they are commonly used to assess the effects of different operational factors on the anaerobic digestion process. Hydrolysis of particulate material is often assumed to be the rate limiting step in anaerobic digestion. Its velocity is often estimated by data fitting from batch tests. In this study, a Monod-type alternative to the commonly used first-order approach is presented. The approach was adapted from balancing a continuously stirred-tank reactor and better accommodates the fact that even after a long incubation time, some of the methane potential of the substrate remains untapped in the digestate. In addition, an equation is proposed to directly calculate the hydrolysis constant from the time when the daily gas production is less than 1% of the total gas production. The hydrolysis constant can then easily be read-off from a table when the batch test duration is known.

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1. Introduction

Anaerobic batch tests are considered state of the art for the determination of methane yield potential of substrates, which are of great relevance for the design and operation of digesters treating sewage sludge [1], biowaste [2], and agricultural material [3]. As batch tests are easier to conduct than continuous experiments, they are also often used to evaluate the effects of different conditions such as certain types of pre-treatment on the overall anaerobic digestion process efficiency [4,5].

Already in 2006, the Association of German Engineers (VDI) published the guideline VDI 4630 "Fermentation of organic materials, Characterization of the substrate, sampling, collection of material data, fermentation tests" [6]. Besides characterization of substrates and sampling and sample preparation, the guideline also provides methodology for fermentation test in batch as well as in continuous procedures. By now, the guideline attracts interests in the international community too and builds to base for

many experiments [7–13]. When performing a batch test, the question when to terminate the experiment is crucial. The VDI 4630 addresses to this problem by introducing the so-called 1% criterion, which pretends to continue the experiment, until the daily gas production is less than 1% of the total gas production [6]. In contrast to any period given, this approach is indeed valid for every substrate. Therefore, an increasing trend of batch experiments is being performed according to this 1% criterion [10,11,13].

In 2009, the "Task Group for the Anaerobic Biodegradation, Activity and Inhibition of the Anaerobic Digestion" of the International Water Association (IWA) proposed a guideline for biomethane potential (BMP) assays in order to consolidate the existing methods and to enhance comparability [14]. The protocol is nowadays the base for most of the experiments performed, ranging from BMP test on the anaerobic digestibility of agricultural sources, such as wheat straw stillage [15], grass land [16], and different manures [17,18], municipal waste activated sludge [19], as well as food wastes [20]. Furthermore, a method was described how to estimate the hydrolysis rate constant from batch data that has been applied in many studies [13,18–24].

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When assuming normal growth (no inhibition, no lack of macro or micro-nutrients), biogas production typically follows a first-order reaction [25,26]. Development of the gas curve is described by two parameters: the ultimate methane production and the time when half of its production is reached. The reciprocal of this half-life is defined as the hydrolysis constant k_h. Both parameters are usually obtained by data fitting from batch tests to inform plant design and process modeling (e.g. with the Anaerobic Digestion Model No. 1, ADM1 [27]).

2. Existing estimation approaches for hydrolysis constants

Hydrolysis of particulate matter to soluble substrates is often assumed to be the rate-limiting step in anaerobic digestion. The hydrolysis constant k_h describes the velocities of degradation and biogas production, respectively. The ultimate methane production should represent the biochemical methane potential (BMP) of the substrate which is theoretically reached after infinite incubation. Several approaches have been proposed in the past to estimate hydrolysis constants and BMP. The following sections evaluate the pros and cons of these approaches.

2.1. The approach of Angelidaki et al. [14] for batch tests

The most commonly used approach to determine hydrolysis constants has been presented by Angelidaki et al. [14]. The authors suggested a first-order kinetic with a methane-based modification in order to relate the decrease of the substrate's chemical oxygen demand (COD) to an increased production of methane:

$$B = B_\infty \cdot (1 - \exp\{-k_h \cdot t\}) \tag{1}$$

where B is the cumulative methane production [l_{CH4}/kg_{VS}], B_∞ the ultimate methane production [l_{CH4}/kg_{VS}], k_h the first-order hydrolysis constant [d^{-1}], and t is the time [d].

The hydrolysis constants k_h can be derived from the slope of plotted experimental data using the linearized version of Eq. (1) as presented in Table 1.

Angelidaki et al. [14] defined the ultimate methane production B_∞ as the cumulative methane production at the last day of the experiment. Unfortunately, no indication has been provided when to terminate the experiment and therefore it is likely that the BMP of the substrate will not be fully captured due to some remaining potential left in the digestate.

2.2. The approach of Eastman and Ferguson [28] for CSTRs

Eastman and Ferguson [28] proposed that the hydrolysis rate function at constant temperature and pH is approximately first order with respect to the remaining amount of degradable particulate COD:

$$r = -k_h \cdot F \tag{2}$$

where r is the hydrolysis rate [$g/(l \cdot d)$]; k_h the first-order hydrolysis constant [d^{-1}], and F the concentration of degradable particulate COD [g/l].

In a completely mixed, continuous-flow reactor at steady state, a mass balance on particulate COD yields [28]:

Influent particulates – Effluent particulates – Rate of hydrolysis
$$= 0$$

or expressed as an equation (Assumption: $Q_{in} = Q_{out} = Q$):

$$Q \cdot F_0 - Q \cdot F - k_h \cdot F \cdot V_R = 0 \tag{3}$$

where Q is the hydraulic flow rate [l/d], F_0 the influent concentration of degradable particulate COD [g/l], and V_R is the reactor volume [l].

By introducing the hydraulic retention time θ

$$\theta = \frac{V_R}{Q} \tag{4}$$

the following is obtained:

$$0 = Q \cdot (F_0 - F - F \cdot k_h \cdot \theta) \tag{5}$$

For $Q \neq 0$, the following equation can be used to describe the change of the concentration of degradable particulate COD in the reactor [28]:

$$F = \frac{F_0}{1 + k_h \cdot \theta} \tag{6}$$

The hydrolysis constants k_h and the degradable particulates F_0 can be found from the slope and the intercept of plotted experimental data using the linearized version of Eq. (6) as presented in Table 1 [29].

In order to determine the hydrolysis rate constant k_h and the degradable particulates F_0 of domestic primary sludge, Eastman and Ferguson [28] carried out four identical continuous digestion experiments, but each with a different retention time. As soon as steady state was reached (based on selected stable parameters for at least three retention times), total particulate COD utilized ($F_0 - F$) was measured in every reactor. Subsequently, the data were plotted according to Table 1 in order to calculate k_h and F_0 from the data fit.

The retention times applied were 9, 18, 36, and 72 h. Together with the concentration of volatile solids (VS) of 26.6 g/l in the influent sludge, the resulting organic loading rate (OLR) can be calculated using the following relationship:

$$OLR = \frac{c_{VS}}{\theta} \cdot 24 \frac{h}{d} \tag{7}$$

where OLR is the organic loading rate [$g_{VS}/(l \cdot d)$], c_{VS} the concentration of volatile solids in the influent [g/l], and θ is the hydraulic retention time [h].

For the given retention times, OLRs between 71 $g_{VS}/(l \cdot d)$ (9 h) and 9 $g_{VS}/(l \cdot d)$ (72 h) have been applied. The rather short retention times and high loading rates, respectively, are reflected in the very low specific gas production reported (Table 2).

Table 1
Determination of k_h by linearized version of Eqs. (1), (6), and (11).

Eq.	Linearization	Ordinate	Abscissa	Slope	Intercept
(1)	$\ln\left(\frac{B_\infty - B}{B_\infty}\right) = k_h \cdot t$	$\ln\left(\frac{B_\infty - B}{B_\infty}\right)$	t	$-k_h$	–
(6)	$\theta = F_0\left(\frac{\theta}{F_0 - F}\right) - \frac{1}{k_h}$	θ	$\frac{\theta}{F_0 - F}$	F_0	$-\frac{1}{k_h}$
(11)	$\frac{1}{t} = k_h \cdot F_0 \cdot G \cdot \frac{1}{B} - k_h$	$\frac{1}{t}$	$\frac{1}{B}$	$k_h \cdot F_0 \cdot G$	$-k_h$

Table 2
Operational parameters of continuous-low experiments carried out by Eastman and Ferguson [28]. Organic loading rates were calculated according to Eq. (7).

Detention time (h)	Organic loading rate ($g_{VS}/(l \cdot d)$)	Gas production ($g_{COD}/l_{Inf.}$)
9	71	0.06
18	35	0.14
36	18	0.21
72	9	0.28