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The Kinetics for Mathematical Modelling on the Anaerobic Digestion of Organic Waste- A Review

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Anaerobic digestion is a biological process that could provide high valorisation value of waste by producing biogas as a form of renewable energy and the digesate as biofertiliser. A mathematical model is an essential tool to observe, predict, simulate and optimise the system's behaviour at different conditions. The modelling approach for wet digestion and dry digestion is different due to the presence of solid content. The selection of the limiting step for modelling can be influenced by both substrate and microbial loadings. The complex substrate is heterogenous by nature and consists fractions of organic matter with different biodegradability. The formulation of the model is affected by the type of substrates and its characteristic, which exhibits different substrate degradation kinetics, intermediate production and consumption behaviour and the biogas production. This review aims to look at the rationalisation and findings that lead to the different formulation of the models, from the point of view of the variation of the organic waste, including municipal solid waste, food waste and animal manure. Recent research results for the anaerobic digestion of organic waste is also discussed, which serves to provide better insight for future generalisation of a model.

1. Introduction

Anaerobic digestion (AD) is a biological treatment that could realise the waste-to-energy concept. The organic waste undergoes several parallel and sequential processes to produce the end-product, biogas, which can be transformed to renewable energy. The main steps in AD include hydrolysis, acidogenesis, acetogenesis and methanogenesis. The use of AD for treating wastewater has been well-established as compared to the AD of complex substrates (Momoh et al., 2013), such as municipal solid waste (MSW), which is heterogenous in nature and varied along season and geographical location.

Mathematical model is a set of mathematical equations that can represent the main aspects of a biological system, formulate and predict the system's behaviour under different conditions (Donoso-Bravo et al., 2011), quantify the empirical behaviour and simulate the system (Eposito et al., 2008), predict the most influential process variable in the system (Fdez-Güelfo and Álvarez-Gallego, 2011) and to identify elements for optimisation (Lauwers et al., 2013). The current mathematical models can be divided into several generations as stated by Donoso-Bravo et al. (2011).

The first-generation models were modelled based on either hydrolysis or methanogenesis as the limiting step. The second-generation stressed on the intermediate products and their influences over the AD process. The third-generation of models incorporated inhibition species on the microbial activities and the consideration of different substrates used in AD. Some of the popular models found in literature incudes the anaerobic digestion model 1 (ADM1), first-order kinetic model, Gompertz model and their modifications. For example, the use of the first-order model for degradation kinetics and the use of modified Gompertz equation for simulating biogas accumulation (Nielfa et al., 2015). There are several new approaches on the modelling for complex substrates, where focus have been paid on the role and observation of microbial adaptation, the effect of different substrate to microbe (S/M) ratio, total solid (TS) content, two-phase or three-phase substrate interaction and more.

The mathematical modelling for AD of a complex substrate is challenging due to the complicated nature of the technology itself and the substrate. In complex substrates, the particulate substrate is first disintegrated into

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macromolecules, such as carbohydrates, proteins and lipids. These will then hydrolyse to simple sugars, amino acids, and long-chain fatty acids (LCFA) which are then converted to fatty acid, acetate, H_2 and CO_2 via acidogenesis. The acetate from acetogenesis will then be converted to CH_4 by methanogenesis (Bollon et al., 2011). The intermediary reaction mechanisms for biogas production requires more understanding but experimental studies are complicated as the biogas production is affected by many process parameters (Rajendran et al., 2014). These parameters include the type of substrate, type of microbial inoculant (MI), the substrate to MI (S/M), total solid (TS) content, organic loading rate (OLR), pH and more.
Lauwers et al. (2013) performed a review on the mathematical modelling of AD of biomass and waste. The paper focuses on discussing the power and limitation of a mathematical model, including ADM1, and concluded microbial community data and black-box model can be used to further improve the model performance. Kythreotou et al. (2014) performed a review of simple to scientific models for AD, stating exclusion of critical parameters from the model limits the model's accuracy. The paper concluded that identifying rate-limiting step and the intermediate fermentation products is crucial but challenging for the AD of complex substrates. Both reviews highlighted the important role of the inclusion of microbial interactions for further improvement on model's performance. In this paper, the mathematical models focusing on complex organic waste, including municipal solid waste (MSW), food waste (FW) and manures, is being reviewed and discussed. Recent findings related to the substrate, intermediates and products were presented which can be used to improve the model. One of the highlight of the paper is that the point of discussion is based on the categorisation of waste (MSW, FW and manure) rather than based on the characterisation of mathematical model (for example, mechanistic, empirical, first-order, ADM1 and more), which allows a better insight on the suitability of different models in respective to the waste type.

2. Methodology

This review is based on a literature search using ScienceDirect with the focus on several keywords: mathematical model for anaerobic digestion on organic waste, mathematical model for anaerobic digestion on solid waste, mathematical model for anaerobic digestion on food waste, kinetic on anaerobic digestion of organic waste, kinetic on anaerobic digestion on solid waste and kinetic on anaerobic digestion on food waste.

3. Mathematical modelling for AD of complex substrate

Mathematical modelling for AD of complex substrate is different from wastewater due to several reasons as identified by Momoh et al. (2013), which included:
(1) The unsuitability of modelling approach based on maximum specific growth rate coupled with a short hydraulic retention time (HRT) for complex substrate.
(2) Challenges in differentiating between bacteria volatile suspended solid (VSS) and complex biomass VS.
(3) A non-soluble form of complex substrate
(4) Presence of recalcitrant fraction
(5) Heterogenous nature of the complex substrate.

3.1 The limiting steps

Anaerobic digestion (AD) can be divided into two categories, based on the total solid (TS) content of the medium: the wet digestion with less than 15 % TS and the dry digestion with more than 15 % TS (Mata-Alvarez et al., 2000). The kinetic model between wet digestion and dry digestion is different due to the presence of particulate matter and high solid content, which affect the rheological behaviour, chemical equilibria and mass transfer (Bollon et al., 2011).
Hydrolysis is considered as the main limiting step in many studies. Hydrolysis has been traditionally modelled using the first-order kinetics. Fractionisation of an organic pool is gaining interest in the modelling for a complex substrate, which includes fractions with different biodegradability, including hardly degradable material (Vavilin et al., 2008). The disintegration step and hydrolysis step are often modelled by first-order kinetic (Bollon et al., 2011). However, due to the difference in experimental conditions, hydrolytic biomass to substrate ratio and the lumped effect of disintegration and hydrolysis, different kinetic coefficients for the first-order hydrolysis rate were reported (Vavilin et al., 2008). Substrate characterisation should be divided into carbohydrates, proteins, lipids and the inert fraction with the disintegration or hydrolysis as the limiting step (Galí et al., 2009). In terms of the degradation kinetics of the macromolecules, carbohydrates are degraded first as the preferable substrate for the microbes. Protein and lipid had slower degradation kinetics and occurred after microbial acclimatisation has taken place (Nielfa et al., 2015).
Myint et al. (2007) studied on the modelling during the dry digestion of cow manure residues in a leach-bed reactor. The model displayed two distinct segments which were due to the presence of two components in the

substrate: a readily degradable fraction, the hemicellulose and the slowly degradable fraction, the cellulose. The rate of hydrolysis is dependent on the surface area of the particles occupied by the organisms, which included both the native microbes from the manure and the introduced microbes as an inoculant. Hydrolysis efficiency in AD should consider the complex interaction between the different biomass species and intermediate products, with their relative spatial distribution (Vavilin et al., 2008).
Acidogenesis is modelled based on the assumption that the acidogenic biomass grows on the soluble products of hydrolysis. The growth of the biomass is modelled as a single biomass, which is the acidogens, that feeds on the hemicellulose and cellulose at a different kinetic constant (Myint et al., 2007). The acidogenesis is governed by the respective microorganisms that convert the hydrolysates to several acids. The acidogenenic biomass can be integrated into one which the growth is represented by the Monod equations (Bollon et al., 2011).
Methanogenesis may be more accessible from the perspective of monitoring as it has a slower happening rate than acidogenesis and acetogenesis. The sum of all gas compounds produced during the process and pH are the most widely used parameters for modelling application. Accumulation of CH_4 can be modelled by Monod model when acetoclastic methanogenesis is the rate-limiting step, provided that there is no inhibition at high OLR or high organic solids to inoculum ratio (Vavilin et al., 2008). Figure 1 shows the possible consideration to be included in the mathematical model and kinetic study when there is variation in the digestion type (wet or dry), substrate type (mixed, segregated, heterogenous, homogenous), the production and possible inhibition of intermediates products and lastly, the production and accumulation of biogas or CH_4.

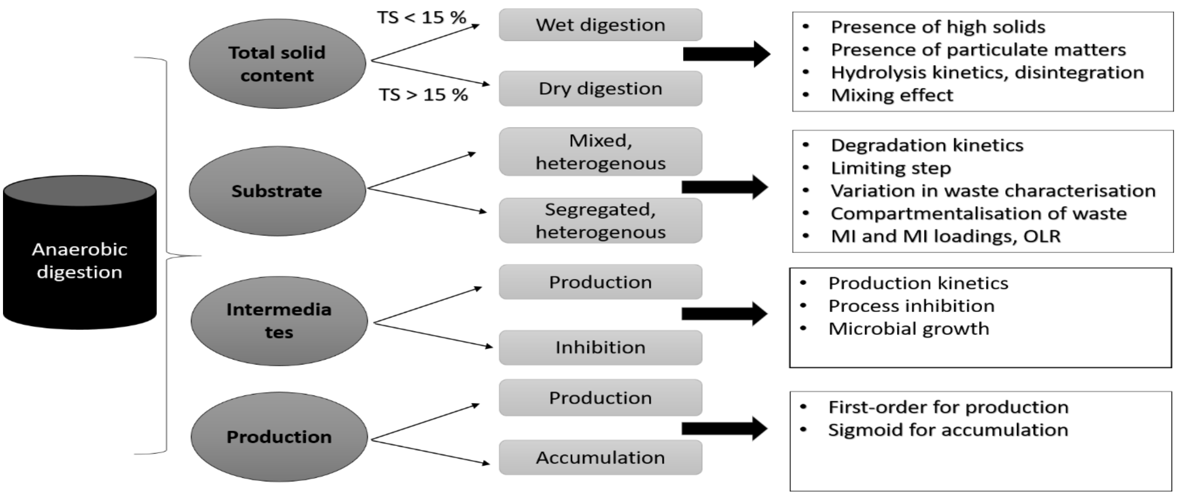

Figure 1: Considerations affecting the formulation of mathematical model following changes in digestion system, substrate, intermediates and gas production.

3.2 Type of organic waste, degradation kinetics and mathematical model

3.2.1 Municipal solid waste

The organic fraction of municipal solid waste (OFMSW) is heterogenous and composed of different waste with different biodegradability (Nielfa et al., 2015). The hydrolysis is the limiting factor in a high-solid system. In the case of OFMSW, the hydrolysis rates differed among different particulate components and microbes prefer one substrate over the other.
Sun et al. (2013) modelled on the co-digestion of municipal biowaste (MBW) and waste activated sludge (WAS). The model included disintegration process, kinetic rate equations for soluble components, hydrolysis process, acid production process, H_2 production process and CH_4 production process. At high OLR, methanogenesis is the rate-limiting step due to the decrease in pH and accumulation of VFA, which inhibit methanogenic activity. At low OLR, hydrolysis is the main limiting step which is dependent on the substrate concentration and followed a first-order reaction.

3.2.2 Food waste

Food waste (FW) is one of the best substrate for anaerobic digestion (AD) due to its CH_4 production potential (Zhang et al., 2011). FW has several characteristics: high volatile solid (VS), high moisture, low pH and high in carbohydrate, protein and lipid. The mono-digestion of FW often encounters restriction at high loading due to rapid hydrolysis and subsequent acid accumulation. Liu et al. (2009) identified the food to microorganism (F/M) ratio as the most critical feature in the degradation of VS of organic solid particles. The choice of type of MI and the S/I ratio influences the substrate degradation kinetics and VFA production (Bong et al., 2017). Durruty et al (2013) proposed a model to evaluate the effect of organic fractions on biogas generation from potato residues. The organic fractions are divided into inert and biodegradable fractions, where each fraction can be further divided into soluble and particulate fractions.

Dhamodharan et al. (2015) did a kinetic study on the AD of FW using seven animals dungs. The study illustrated the effect on the choice of MI and the food to microbes (F/M) ratio on CH_4 production. Among the seven animal dungs, pig dung and cow dung exhibited highest CH_4 production and VS destruction. The use of high F/M ratio in high solid AD allows a successful digestion without the need of pH adjustment due to the presence of a large amount of inoculant. But in the case of FW, low F/M ratio is preferable as FW is easily hydrolysed. The presence of a large amount of inoculant will lead to rapid degradation and subsequent acid accumulation, which inhibit the methanogenesis. This is similar to Motte et al. (2013) who stated the difference in modelling approach based on solid to microbial biomass (S/X) ratio. For lab work, high S/X ratio is preferable to observe the changes in a microbial community. For industrial, low S/X ratio is preferable to prevent process failure as high S/X ratio requires relatively longer adaptation and monitoring period.

Wang et al. (2014) studied on the kinetics of FW under acidic conditions with two types of MI: aerobic activated sludge and anaerobic activated sludge. Hydrolysis of FW increased when anaerobic activated sludge was used at any pH. Among the macromolecules, the microorganisms preferred carbohydrates and it was first degraded to glucose than to pyruvate (Chen et al., 2013). Following next is the degradation of the protein, which can be categorised into two stages: the dissolution of protein at an early stage and then transformation at a later stage. The VFA profile is observed to be different. Acetate and butyrate dominated during hydrolysis of carbohydrates where acetate, propionate and butyrate dominated from protein and lipid hydrolysis.

In the study by García-Gen et al (2015), they improved the ADM1 model by incorporating an extra disintegration-hydrolysis step during the AD of individual fruits and vegetable wastes (FVW). The model considered the disintegration kinetics for readily and slowly biodegradable fractions. The disintegration-hydrolysis involved the breakdown of the OM with a conglomerate of macromolecules into the soluble macromolecules that can then be hydrolysed by the microbial enzymatic activities. This step has known to be the limiting step for solid AD.

Poggio et al (2016) proposed a novel model based on the ADM1 model for describing the AD of FW and GW. The model assumed that the OM is made of a mixture of particulate and soluble fractions and subdivided them into four substrate fractionation models. The study concluded that model with one particulate and one soluble fraction is the best suitable for FW whereas the model with two particulate fractions is best fitted for FW. Particulate fractions have hydrolysis as limiting steps thus is described by the first order kinetics. Particulate fraction is further divided into readily and slowly degradable fractions. Soluble fractions are directly assimilated by microbes thus its kinetic is influenced by biomass concentration and their respective uptake rates.

During the AcoD of FW and pig manure (PM) by Dennehy et al (2016), the authors proposed a dual pool first order model and compared with a conventional first order model and a Gompertz model. The new model incorporates a new parameter which is the ratio of rapidly degradable substrate to a total degradable substrate to capture the kinetics resulting from the labile fraction of FW. It showed that the newly developed model provided the best fit for the study of codigestion of FW and pig manure (PM) under different mixing ratio, which is 1/0, 4/1, 3/2, 2/3, 1/4 and 0/1. The dual pool model takes into the consideration of two hydrolytic constants, which is for the fast degradable and a slowly degradable substrate. The test of fitness showed that the first-order model is suitable to determine the rate of hydrolysis provided there is no inhibition of VFAs. The first order model failed to capture the CH_4 yield as most the CH_4 was generated in the first five days. The Gompertz model performed slightly better but the accuracy greatly decreases when the mixing ratio of PM: FW is 0:1 and 1:4, when the PM proportion is high.

3.2.3 Manure and digestate

The scale of the digester can influence on the effect of parameters. Hulle et al. (2014) studied the kinetic on AD of cow manure between lab scale (3.78 L) and pilot scale (120 L). The study concluded that mixing and VFA accumulation have a great effect on the formulation of the model. The experiment work showed a significant increase of VFA concentration during the non-mixing period. Modelling of pilot scale system should include the effect of mixing to prevent overestimation, account for VFA accumulation and reduce the need for model calibration.

Some models focus on the loss of material, for example, NH_3, during the storage of the digestate. Whelan et al. (2010) studied on the non- steady state partitioning model for describing NH_3 volatilisation during storage of the digestate. The model was able to describe the behaviour of NH_3 well in the digestate, where NH_3 loses is linear with time and open storage could result in significant losses of NH_3 as compared with covered facilities,

especially those with a high depth to surface area ratio. There is a need to consider bacterial adaptation for modelling of the AD of complex biomass (Momoh et al., 2013).
Figure 2 illustrates a summary which maps the possible selection of limiting step and the parameters following different choices of organic waste and input.

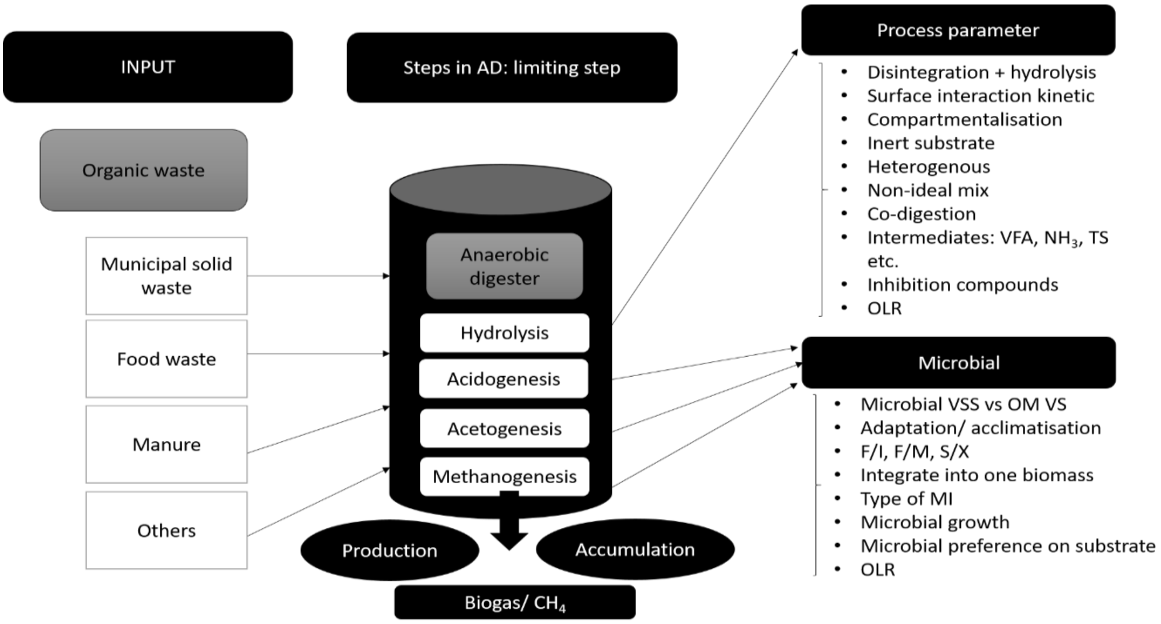

Figure 2. The relationship among the type of organic waste, limiting step and parameters for modelling the kinetics of complex substrate.

4. Conclusion

Mathematical modelling and kinetic study for the anaerobic digestion (AD) of complex organic waste would require further insights. The main kinetic model includes ADM1, first order and Gompertz model whereas Monod model remains the main stream for modelling AD biomass. This paper reviewed several modelling works on the AD of complex organic waste and the effect on microbial loadings, which can influence the suitability of the model in describing and predicting the system behaviour. For the modelling of complex organic waste, including municipal solid waste (MSW), food waste (FW) and manure, the following should be integrated to the model:
(1) The parameter "fractionisation" should be included due to the presence of organic pool with different biodegradation kinetics, including a separate pool for inert materials. It is useful to apply on MSW where there is a mixed of waste, including food waste with labile OM and green waste with high cellulosic content.
(2) Hydrolysis as the rate limiting step is influenced by the surface-interaction kinetics and the parameter "disintegration" should be added prior to the hydrolysis step.
(3) Methanogenesis could serve as the rate limiting step at low loading where there is no acid inhibition on CH_4 production due to the rapid degradation of labile organic matter, such as when FW is used as the sole feedstock.
(4) The role of microbial inoculant, its loading amount and its adaptation capability would require better study to allow a better integration with the currently available generalised kinetic models, such as first-order and Gompertz.
(5) The difference between the modelling assumption between wet and dry digestion, bench scale and pilot scale should be considered, due to the presence of high solid content, non-ideal mixing and possible process failure due to VFA accumulation at non-ideal mixed AD plant at high loadings.

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