A modified anaerobic digestion process with chemical sludge pre-treatment and its modelling

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ABSTRACT

Activated Sludge Models (ASMs) assume an unbiodegradable organic particulate fraction in the activated sludge, which is derived from the decay of active microorganisms in the sludge and/or introduced from wastewater. In this study, a seasonal change of such activated sludge constituents in a municipal wastewater treatment plant was monitored for 1.5 years. The chemical oxygen demand ratio of the unbiodegradable particulates to the sludge showed a sinusoidal pattern ranging from 40 to 65% along with the change of water temperature in the plant that affected the decay rate. The biogas production in a laboratory-scale anaerobic digestion (AD) process was also affected by the unbiodegradable fraction in the activated sludge fed. Based on the results a chemical pre-treatment using H2O2 was conducted on the digestate to convert the unbiodegradable fraction to a biodegradable one. Once the pre-treated digestate was returned to the digester, the methane conversion increased up to 80% which was about 2.4 times as much as that of the conventional AD process, whilst 96% of volatile solids in the activated sludge was digested. From the experiment, the additional route of the organic conversion processes for the inert fraction at the pre-treatment stage was modelled on the ASM platform with reasonable simulation accuracy.

Key words | mathematical model, partial chemical oxidation, pre-treatment, sludge constituents, sludge minimisation

INTRODUCTION

Anaerobic digestion (AD) is one of the most commonly used processes to decompose waste activated sludge (WAS) in municipal wastewater treatment plants (WWTPs) since it makes it possible to reduce sludge mass for final disposal whilst recovering biogas. Nevertheless the digestion efficiency in most conventional AD processes is still limited to about 50%, and hence significant efforts are being made to improve the performance. For this challenge, two engineering approaches are currently focused (Appels et al. 2008). One is to classify the sludge constituents by modelling its biodegradability (Nopens et al. 2009) and the other is to develop sludge pre-treatment techniques to change the sludge properties for improving the decomposition (Bougrier et al. 2007; Braguglia et al. 2012).

With respect to the distinction of organic particulates in the sludge, concepts of mathematical models developed by IWA task groups can be used (Activated Sludge Models (ASMs) by Henze et al. (2000) and Anaerobic Digestion Model No.1 (ADM1) by Batstone et al. (2002)). The particulates are classified into unbiodegradable particulates (XU), sets of active biomass (XBio) and sets of slowly degradable materials (XCB). For the pre-treatment of sludge, depending on the methods applied, the XU fraction may change to XCB leading to a high theoretical digestion efficiency whilst a conversion of XBio to XCB may enable high digestion rate in the AD process. Apart from ADM1, the hydrolysis step of XCB (solubilisation) has been traditionally assumed to be rate-limiting of the entire reaction (Eastman & Ferguson 2000).
However recent studies suggested that anaerobic decay of the ordinary heterotrophic organisms (X_SOHO) in the WAS influenced the digestion efficiency, which was given from an analogy of ASMs (Sötemann et al. 2005; Yasui et al. 2006). In the assumption, X_SOHO decays anaerobically and is converted to XC_B and X_U with a fixed stoichiometry of f_XU (production of inert materials from decay). The produced XC_B is then quickly hydrolysed by the microorganisms present in the AD process where low molecular weight substrates are eventually formed. In this way, the model, which is an extension of the ASM concept, expresses Eastman’s ‘hydrolysis’ as a combined reaction of bacterial death and its external decomposition. Accordingly, the keys to estimate the digestion efficiency of AD processes would be the ratio of X_U to total WAS organic (X_Org), X_SOHO’s specific decay rate and the conversion of X_U to XC_B.

Based on the above theoretical consideration, when state variables from the sludge pre-treatment module are mapped in the AD process, the impact of the module would be calculated in a mathematical manner. Hence a study to engage the improved biogas production system with modelling the sludge conversion process will help to elucidate optimisation of the process configuration and the selection of the appropriate pre-treatment methods. To progress the study, a laboratory-scale conventional AD reactor (digester) was operated for 1.5 years using the WAS having an annual change of X_U/X_Org ratio, and the digestion performance was contentiously monitored. The performance was compared to that from the modified AD reactor equipped with a chemical sludge pre-treatment module (advanced oxidation process). The two process responses were then simulated using an extended ASM with a set of new state variables produced from the sludge pre-treatment.

MATERIAL AND METHODS

Estimation of X_U fraction in the WAS

WAS was collected at about 2-week intervals from Kogasaki WWTP, Japan, where a conventional biochemical oxygen demand (BOD) removal process was operated at 5-d sludge retention time (SRT). The collected WAS (ca. 6,000 mg total volatile solids (TVS) per litre, 9,000 mg chemical oxygen demand (COD) per litre) was immediately used for the batch tests to estimate X_U fraction under aerobic condition. Unlike a typical ASM procedure (Henze et al. 2000), the tests were carried out under 35 °C, which was a comparable temperature to that of a typical mesophilic AD process. Together with the aerobic tests, tests under anaerobic condition were also conducted in order to check consistency of the WAS constituents. For the aerobic test, 450 mL of the WAS was placed into a gas-tight 0.5 L medium bottle with addition of 20 mg/L of allylthiourea to inhibit oxygen uptake by nitrifiers. The percentage of individual WAS constituents (X_U, X_SOHO and XC_B) were estimated focusing on the chronological response of oxygen uptake rate (OUR) that was attributed to the decay of X_SOHO and degradation of XC_B. The OUR was logged at every 10 min for 5–7 days using a respirometer with an automatic oxygen gas supply system and a strong stirring base (AER-8, Challenging Systems, Inc., USA). For the anaerobic tests, fresh anaerobically digested sludge was simultaneously taken from a mesophilic anaerobic digester at Hiagari WWTP, Japan, and its 450 mL (ca. 10,400 mg-TVS/L, 17,400 mg-COD/L) was mixed with 50 mL of the WAS. The mixture was incubated under 35 °C for 5–7 days whilst methane gas production rate (MPR) was logged at every 30 min using the respirometer without feeding oxygen. By subtracting the MPR of the blank test without addition of WAS from that of the tests, the net MPR was obtained. Due to low food:microorganism ratio of the tests, accumulation of volatile fatty acids was negligible over the incubation periods and hence the net MPR could be directly interpreted as the particulate degradation rate of the WAS.

Continuous AD test

Conventional AD process

A laboratory-scale continuous anaerobic digester with a working volume of 1.8 L was operated as a conventional AD process with chemostat mode at 35 °C. The WAS collected at 7–10 day intervals from Kogasaki WWTP was immediately centrifuged to about 20,000 mg-COD/L and stored at 4 °C. The digester was fed with the WAS every day at 36 days of hydraulic retention time. Methane gas production from the digester was continuously logged using a gas counter after passing it through caustic pellets to remove CO_2 in the biogas (MGC-1, Litre Meter Limited, UK).

Modified AD process equipped with the pre-treatment module and solid/liquid separation unit

As illustrated in Figure 1, another digester with a working volume of 8.0 L equipped with a pre-treatment module and a centrifugal solid/liquid separation unit was installed.
The solid/liquid separation unit worked to extend the biological reaction time in the digester. According to Yasui et al. (2005), even with SRT longer than 60 days, the X_U fraction in WAS was barely biodegradable. Hence the process configuration was appropriate to evaluate the biological degradation of the materials from the pre-treatment. Throughout the operation, a part of the liquor in the digester was manually transferred to the centrifugal solid/liquid unit and its supernatant was discharged. The rest of the portion (thickened digestate) was pumped to the digester. During the solid/liquid separation, a small amount of organic cationic polymer flocculants (0.034 g-polymer/g-TS (total solids)) was added after 120 days of the start-up in order to reduce loss of the suspended solids to the supernatant. The digester was operated for 1.5 years under a volumetric loading rate of about 0.55 kg-COD/(m^3·d) on the basis of solids)) was added after 120 days of the start-up in order to reduce loss of the Fe materials to the supernatant was negligible materials seemed to be mostly precipitated in the digester, the inuent WAS.

For the pre-treatment process, a Fenton-like reaction was applied in which H_2O_2 and Fe ions produced radicals that partially decomposed the complex components in the sludge (e.g. Fe^{2+} + H_2O_2 + [H] → Fe^{3+} + OH^- + OH^- + [H] → Fe^{3+} + 2OH^- + H^+; Fe^{3+} + H_2O_2 + [H] → Fe^{2+} + H^+ + OOH^- + [H] → Fe^{2+} + 2H^+ + OH^- + 0.5O_2). The digestate to be treated was taken from the digester at 3-d intervals which corresponded to 0.016 d^{-1} of specific recycle rate. Ferrous chloride (FeCl_2) was dosed in the initial phase but it was discontinued when the Fe materials in the digester accumulated to be about 5 g/L, in which the molar ratio of Fe:H_2O_2 became slightly more than 1:1. As the Fe materials seemed to be mostly precipitated in the digester, loss of the Fe materials to the supernatant was negligible during the experimental period (<2 mg-Fe/L in supernatant). The H_2O_2 dose was set at 0.03-0.04 g-H_2O_2/g-TVS on the basis of the sludge mass to be treated. A H_2O_2 solution (30 wt%) was slowly mixed with the digestate for about 10-20 min. The pre-treatment temperature was set at 80 °C without pH control, and the pre-treated sludge was stored at 4 °C for 24 hours before returning to the digester.

### Analytical procedures

#### Chemical composition of sludge

Total and soluble volatile solids (VS) and COD concentrations were measured according to #2540 and #5220.D in Standard Methods (APHA 2005), respectively. The supernatant obtained from the solid/liquid separation unit was filtered using glass filter (Whatman GF/F). Concentration of carbohydrates (total sugar) and peptide bonds (proteins) in the filtrate were analysed using the phenol-sulphuric acid method (Dubois et al. 1956) and microbiuret method (Itzhaki & Gill 1964) respectively. The concentration of polyphenolic compounds (humic substances) in the filtrate was estimated by subtracting the value measured by microbiuret method from that measured by Lowry-Folin method, which was more sensitive on phenolic groups than proteins (Lowry et al. 1951). Glucose, egg albumin and alkali-extracted lignin were used for the standards for total sugar, peptide bonds and polyphenolic compounds respectively (Kishida Chemicals, Japan).

#### Dynamic simulation

Dynamic simulations of the two continuous experiments were performed focusing on chronological changes of the methane production and volatile solid concentration in the digesters. For this purpose GPS-X ver.6.3 (Hydromantis Environmental Software Solutions Inc., Canada) was used. The reaction map developed is shown in the later section using standardised notation by Corominas et al. (2010).

### RESULTS AND DISCUSSION

#### The impact of X_U fraction on the AD of WAS

As shown in Figure 2(b), the X_U fractions in WAS COD (X_U/X_Org) in the aerobic tests showed a sinusoidal response varying from 40 to 65% with a half-width of 0.5 year according to the change of water temperature at the WWTP. The lowest X_U/X_Org ratio (40%) was observed when water temperature was also a minimum at 14 °C, whilst the highest X_U/X_Org ratio (65%) was seen in high water temperature, suggesting more decay took place. The plots of X_U/X_Org ratio in the aerobic tests showed a comparative pattern to those in the anaerobic tests, and its regression with the anaerobic dataset was y = 0.99x (r^2 = 0.83) (data not shown). These indicated that X_U/X_Org ratio based on the
ASM concept could be direct information to estimate the AD efficiency of the WAS.

Based on the results, a dynamic simulation of MPR and TVS concentration for the conventional AD process was conducted where 0.21 d⁻¹ of anaerobic specific decay rate for X_{OH} was applied, which was the average in the batch anaerobic tests. Both MPR and TVS concentration in the digester were successfully simulated, as shown in Figure 2(c) and 2(d) respectively. Therefore the X_{U}/X_{ORG} ratio was thought to be one of the most influential factors on the digestion performance. Although the MPR fluctuated due to fluctuation of the influent WAS concentration over the experiment, on average about 33% of the WAS COD was converted to methane, as shown in Figure 2(d).

The digestion efficiency of the modified AD process

For the modified AD process equipped with the pre-treatment module, as shown in the left graphs of Figure 3 in which the dynamic simulations were also drawn, the conversion of WAS to biogas was remarkably improved. Throughout the experimental period of 1.5 years, a precise COD mass balance was obtained as shown in the right graph of the figure. Between 70 and 80% of WAS COD was converted to methane whereas 16–26% of the WAS COD was retained in soluble materials, depending on the H₂O₂ dose at the pre-treatment. The remaining particulate COD in the graph was attributed to the sludge sampling for the chemical analysis and the loss in the effluent stream. On average, about 96% of TVS compounds in the WAS was digested to gaseous and/or liquid form with the experiment for H₂O₂ dose at 0.04 g-H₂O₂/g-TVS. The methane conversion efficiency slightly decreased under the operation when H₂O₂ dose was reduced to 0.03 g-H₂O₂/g-TVS, suggesting that H₂O₂ dose affected the conversion stoichiometry of X_{U} to biodegradable materials.

The chemical analysis of the soluble fraction revealed that the dominant soluble COD of the supernatant was polyphenolic compounds accounting for 52.4% of the total whereas 11.4% of COD was detected as sugar and 16.2%
as proteins respectively. Twenty per cent of COD was retained as unidentified fraction. As the BOD concentration of the supernatant was a negligible level (data not shown), most of the soluble COD was thought to be unbiodegradable organics ($S_U$). Since monomer sugar and normal proteins are supposed to be biodegradable, the results suggested that the $S_U$ molecules were quite complex. A future study to compare the molecule structure with that of ordinary $X_U$ might give chemical insights for the refractory organics.

The development of a process model

For the reaction map as shown in Figure 4, the oxidant ($H_2O_2$, $S_{Oxidant}$) was assumed to convert the COD particulates (composite, $X_{Org}$) in the sludge into two kinds of slowly hydrolysable materials ($X_{CB_Ss}$ and $X_{CB_Su}$) leading to substrates ($S_{SS,ACO}$) for acidifiers and soluble unbiodegradable organics ($S_U$) respectively. The model included two essential additional stoichiometries which depended on the dose and/or type of oxidants, i.e. a loss of COD by the oxidant ($f_{Oxidant}$) and production of inert materials from decay ($f$).

![Figure 3](https://iwaponline.com/wst/article-pdf/69/11/2350/470820/2350.pdf)

**Figure 3** | (a) Methane production rate (NL: normal litre), (b) TVS concentration and (c) the COD mass balance in the modified AD process; ○ – measured, – – simulated.

![Figure 4](https://iwaponline.com/wst/article-pdf/69/11/2350/470820/2350.pdf)

**Figure 4** | Reaction map of the AD process with the pre-treatment module (COD basis). $X_{Bio}$: Microorganisms in WAS, $X_{Org}$: Organic particulates in the AD sludge (composite), $X_U$: Unbiodegradable organic particulates, $X_{ACO}$: Acidogens, $X_{MEO}$: Methanogens, $X_{CB_Ss}$, $X_{CB_Su}$: Slowly hydrolysable materials, $S_{Oxidant}$: Oxidant (negative COD), $S_{SS,ACO}$: Substrate for acidifiers, $S_{SS,MEO}$: Substrate for methanogens, $S_U$: Soluble unbiodegradable organics, $S_{CH4}$: Methane, $f_{Oxidant}$: Loss of COD by the oxidant (-1), $f_{XCB_Ss}$: Production of very slowly hydrolysable materials from the pre-treatment (-1), $Y_{ACO}$: Yield of acidogens (-), $Y_{MEO}$: Yield of methanogens (-).

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oxidant \( (f_{\text{Oxidant}}) \) and an efficiency of the conversion \( (f_{\text{XCB}_{\text{Ss}}}) \). After reacting with the oxidant, the remaining COD in \( X_{\text{Org}} \) was mapped to \( X_{\text{B}_{\text{Ss}}} \) and \( X_{\text{C}_{\text{B}_{\text{Ss}}} \text{Ss}} \) with the ratio of \( (f_{\text{XCB}_{\text{Ss}}}:1-f_{\text{XCB}_{\text{Ss}}} \). Since a considerable \( S_t \) fraction was produced from the modified AD process, its production route was made as \( 1-f_{\text{XCB}_{\text{Ss}}} \). Although the stoichiometry might be affected by the sludge composition of \( X_{\text{Org}} \), for simplification it was assumed that the conversion was a function of only oxidant dose in this study. The \( f_{\text{XCB}_{\text{Ss}}} \) used for the graphs was 0.77 g-COD/g-COD at 0.04 g-H\(_2\)O\(_2\)/g-TVS and 0.60 gCOD/gCOD at 0.03 g-H\(_2\)O\(_2\)/g-TVS respectively.

With respect to the process rate expressions for \( X_{\text{B}_{\text{Ss}}} \) and \( X_{\text{C}_{\text{B}_{\text{Ss}}} \text{Ss}} \), both were assumed to be Contois-type having identical kinetics, which was a comparable structure to that of the hydrolysis of decayed products from WAS organics in ASMs. The kinetics were selected to fit the VS concentration in the digester whilst calibrating the conversion coefficient of \( f_{\text{XCB}_{\text{Ss}}} \) to meet the soluble COD in the supernatant. It appeared that the process rate for the particulate degradation of the pretreated sludge was very low. The maximum specific hydrolysis rate \( (0.8 \text{ d}^{-1}) \) for compounds was remarkably lower than that adapted from ASMs \( (6.0 \text{ d}^{-1}, \text{ at } 35 \text{ } ^\circ\text{C}) \). Also the half-saturation coefficient (1.0 g-COD/g-COD) was much higher than the typical value of 0.055 g-COD/g-COD, suggesting that a first-order type expression could be alternatively applied.

It was noted that sensitivities for the growth-relating parameters and the decay-relating parameters for the two types of anaerobic microorganisms (acidogens: \( X_{\text{ACO}} \); and methanogens: \( X_{\text{MEO}} \)) were low when calculating the sludge concentration in the digestor. This was because the SRT of the digesters was almost fixed over the experiments and the \( X_{\text{B}_{\text{Ss}}} \), \( X_{\text{C}_{\text{B}_{\text{Ss}}} \text{Ss}} \) and \( X_{\text{U}} \) fractions were the dominant particulate COD in the digestor. Consequently literature-based values were roughly adopted for the simulations with stoichiometric coefficients (g-COD/g-COD): \( Y_{\text{ACO}} = 0.14, Y_{\text{MEO}} = 0.09, f_{\text{U}} = 0.08 \); growth kinetics \( (\text{d}^{-1}, \text{mgCOD/L}): b_{\text{ACO},\text{max}} = 4.0, K_{S,\text{ACO}} = 10, b_{\text{MEO},\text{max}} = 0.37, K_{S,\text{MEO}} = 20 \); decay kinetics \( (\text{d}^{-1}): b_{\text{ACO}} = 0.1, b_{\text{MEO}} = 0.1 \) (Batstone et al. 2002; Siegrist et al. 2002).

CONCLUSIONS

Using WAS taken from the municipal WWTP, a kinetic response of the AD processes was studied and the following results were obtained.

1. The fraction of unbiodegradable organic particulates \( (X_{\text{U}}) \) in the WAS showed a sinusoidal curve over a year, having a range between 40 and 65%. The response was almost identical to the seasonal variation of water temperature (14–27 °C) in the WWTP, which was explained by the decay of biomass, leading to both slowly degradable and inert COD, being more predominant at higher temperature. The AD efficiency of the conventional AD process was particularly influenced by the \( X_{\text{U}} \) fraction in the activated sludge fed.

2. When applying \( \text{H}_2\text{O}_2 \) and Fe ions to the sludge pre-treatment as a partial oxidation of \( X_{\text{U}} \), the methane conversion efficiency was improved up to 80%, which was about 2.4 times as much as that of the conventional AD process. On the other hand, a considerable amount of soluble unbiodegradable organics was also built in the system, which accounted for 20% of the activated sludge fed.

3. Based on the dynamic responses of the continuous experiments, a reaction map including anaerobic sludge digestion and pre-treatment was formulated on the ASM platform. The model demonstrated that the improvement of the digestion was attributed to the conversion of the \( X_{\text{U}} \) fraction to biodegradable ones. The production of soluble inert was also calculated. The approach to modelling can be extended in future studies to evaluate system performances for various kinds of modified AD processes with a sludge pre-treatment module.

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