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Development and validation of a simplified model for the anaerobic degradation of phenol
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ABSTRACT

The anaerobic treatment of phenolic wastewater has demonstrated to be a suitable biological system, for that reason, a large number of systems have been implemented in a lab/pilot scale, several industrial plants have also been developed. Despite of this, there is a lack of modeling applications within these systems. In order to enhance the anaerobic treatment of this kind of water, a simplified model of 2 populations and 3 reactions was developed and implemented. The parameter calibration and the model validation were carried out with experimental data obtained from an Anaerobic Sequencing Batch Reactor treating phenolic wastewater through two different operational strategies: sequential batches with a co-substrate and sequential fed-batches without a co-substrate. The model predicted the reactors performance accurately for the different experimental conditions tested. Therefore, the theoretical basis of the model is, in general terms, valid, and its utilization to predict the reactors performance or in control purposes is feasible.

Key words | anaerobic digestion, inhibition, modeling, phenol, wastewater

NOTATION

ASBR Anaerobic sequencing batch reactor
OLR Organic Load Rate
tCOD Total COD
sCOD Soluble COD
pCOD Particulate COD
VFA Volatile Fatty Acid
VSS Volatile Suspended Solids
TA Total alkalinity
PA Partial alkalinity
IA Intermediate alkalinity
HRT Hydraulic Retention Time
\( k_0 \) Hydrolysis catalytic constant (d\(^{-1}\)).
\( S_1 \) Soluble organic matter concentration (g/L).
\( S_2 \) Acetic acid concentration (mmol/L).
\( X_0 \) Suspended organic matter concentration (g/L)
\( X_1 \) Acidogenic biomass concentration (g/L).
\( X_2 \) Methanogenic biomass concentration (g/L).
\( \mu_1 \) Specific growth rate of acidogenic biomass (d\(^{-1}\)).
\( \mu_2 \) Specific growth rate of methanogenic biomass (d\(^{-1}\)).
\( \mu_{1M} \) Maximum specific growth rate of acidogenic biomass (d\(^{-1}\)).
\( \mu_{2M} \) Maximum specific growth rate of methanogenic biomass (d\(^{-1}\)).
\( K_{SA} \) Affinity constant of acidogenic biomass (g/L).
\( K_{SM} \) Affinity constant of methanogenic biomass (mmol/L).
\( K_{F,H} \) Inhibition constant of hydrolysis (g/L).
\( K_{F,A} \) Inhibition constant of acidogenesis (g/L).
\( K_{F,M} \) Inhibition constant of methanogenic (mmol/L).
\( r_0 \) Rate of hydrolysis reaction (d\(^{-1}\)).
\( r_1 \) Rate of acidogenic reaction (g/L d).
\( r_2 \) Rate of methanogenic reaction (g/L d).
IC Inorganic Carbon

INTRODUCTION

Nowadays, anaerobic digestion is considered a consolidated technology due to its important advantages compared to an aerobic process: no aeration is required;
smaller amounts and more stabilized sludge is produced, thus reducing transportation, disposal or treatment costs and finally, the anaerobic biodegradation process produces biogas as a final product and hydrogen as the intermediate product, both of which can be exploited as a source of renewable energy. Its application has been extended to many different substrates from readily degraded organic to recalcitrant organic wastes or an mixture of them.

Several models have been developed in anaerobic digestion, most of them require many kinetic parameters and large systems of differential equations, this is the case for the Anaerobic Digestion Model 1 (ADM1) (Batstone et al. 2002), thus creating difficulties in its use for control purposes (Bernard et al. 2001). Simplified models of two populations, acidogenic and methanogenic, with 2 reactions (Bernard et al. 2001) and 3 reactions (Liu et al. 2008) have been developed thus reducing the number of kinetic parameters considerably. On the other hand, most of the models have been validated with readily biodegradable substrates, such as glucose or ethanol.

Some models have been implemented in the treatment of more complex substrates for example: mixture of fats, proteins, sugars and particulate organic materials (Angelidaki et al. 1999; Batstone et al. 2000a).

Despite the great amount of models, few studies have applied models in the anaerobic treatment of slow degradation compounds which have been treated by anaerobic digestion. This is the case of phenol which already has demonstrated that its treatment by anaerobic digestion, as the sole carbon source or with co-substrates is suitable (Veeresh et al. 2005).

The phenol is a powerful inhibitor for microbial activity. In general, the studies which have modeled the phenol treatment have considered the process as a “black box” using Monod, or Haldane kinetics on the overall process of degradation (Wen et al. 1994; Lin & Lee 2001; Olguin-Lora & Razo-Flores 2004).

A two population model was developed by Jih et al. (2005) which was applied in a UASB reactor with granular biomass. In this model, it was considered that only the acidogenic population was inhibited by the phenol, using a Haldane kinetic, and two reactions where the main pathways of the reaction: phenol, VFAs and Biogas. Although these models or these equations have provided information beneficial to bioreactor operations, the theoretical meaning of kinetic parameter results have been difficult to explain. As has been reported by Fedorak & Hrudey (1984) and by Fang et al. (2006) the initial biotransformation of phenol, which implies the de-aromatization of its stable structure and its transformation to benzoate, is the limiting step of the overall process. Moreover, the phenol probably exerts an inhibition effect over both populations, which is more important when non granular biomass is available.

Continuous reactors (e.g. UASB) must be in operation for long periods of time to attain the necessary steady states at the different operational conditions, to identify the kinetic parameter and to validate any model. The Anaerobic Sequencing Batch Reactors (ASBR), is an anaerobic digestion system which works through consecutive cycles of operation, each of which has the following stages: feeding, reaction, settling, discharge and idle-time. It has been demonstrated that the ASBR operation provided an adequate system in modeling application due to its dynamic and repeatable behavior that can be obtained during the cycles (Batstone et al. 2004).

The aim of this study was to develop and to validate a simplified mathematical model for anaerobic treatment of phenolic wastewater. A 3 reactions and 2 populations model was developed. The kinetic parameters fit and the model validations were carried out with experimental data from two ASBR treating phenolic wastewater.

MODEL FORMULATION

General assumptions and considerations

The model evaluated is based on the model developed by Bernard et al. (2001) but includes the hydrolysis step. To develop and implement the model for the ASBR treatment, some assumptions were made:

- Feeding, settling, discharge and idle time are not considered in the model, since their duration was assumed negligible compared to reaction time and their operational conditions do not facilitate the degradation of organic matter (Bagley & Brodkorb 1999).
Biomass concentration in the reactor at the beginning of each cycle remains constant.

The total concentration of VFA (S2 in Figure 1), composed, mainly, by acetic, propionic and butyric will be considered to behave like acetic.

The complex metabolic pathway of the anaerobic degradation of the phenol is reduced to a process with three reactions: hydrolysis of the phenol (S0 to S1 in Figure 1). In this case, it was called “hydrolysis” to the whole process where the phenol is converted into soluble organic material readily degraded. Some of the involved reactions are: the transformation phenol into benzoate, its de-aromatization and breaking of the ring-structure. Afterwards, the acidification of the hydrolyzed material into volatile fatty acids (VFA) (S1 to S2 in Figure 1). Both reactions are carried out by acidogenic population. Finally, the transformation of VFA into biogas, which is carried out by methanogenic population.

Inhibitory effects on acidogenic and methanogenic population were considered.

All the methane produced exits the reactor through the biogas, so dissolved methane in the liquor reaction is negligible.

### Metabolic pathway and stoichiometry

The acidogenic population hydrolyses the phenol (S0) to soluble material which is suitable to be acidificated (S1) (Equation 1) and, then, it transforms S1 to S2 in the acidogenic process, with microbial growth (Equation 2). Finally, the methanogenic population transform S2 into biogas (CH4 y CO2), with microbial growth (Equation 3).

**Hydrolysis (X1):**
\[ S_0 \rightarrow K_{F_H} S_1 \]  \hspace{1cm} (1)

**Acidogenesis (X1):**
\[ K_{F_A} \frac{S_1}{K_{F_A} + S_0} X_1 + K_2 S_2 + K_{F_A} CO_2 \]  \hspace{1cm} (2)

**Methanogenesis (X2):**
\[ K_3 S_2 \rightarrow X_2 + K_{F_M} CO_2 + K_6 CH_4 \]  \hspace{1cm} (3)

### Reaction rates and inhibitions

Despite of the more complex kinetics have been suggested (Vavilin et al. 2008), hydrolysis was considered as a first order kinetic reaction (Equation 4), as recommended by most studies (Batstone et al. 2002). Although the effect of the phenol on the hydrolysis process has not been reported, a non-competitive inhibition was considered in the model. This kind of inhibition was studied by Vavilin et al. (2008) evaluating the effect of the VFA on the hydrolysis. For acidogenesis, Monod kinetics for growth rate and non-competitive inhibition of phenol was considered (Equation 5). Finally, for the methanogenesis process, a Haldane-like model including the inhibition by VFA (Equation 6) and a non-competitive inhibition by the phenol were considered.

Non-competitive inhibition have been evaluated to model the effect of the other compounds such as LCFA, ammonia and pH on the methanogenic process (Angelidaki et al. 1999; Batstone et al. 2002).

\[ r_0 = k_0 S_0 X_1 \left( \frac{K_{F_H}}{K_{F_H} + S_0} \right) \]  \hspace{1cm} (4)

\[ r_1 = \mu_1 X_1 = \left( \frac{\mu_1 M'}{K_{SA} + S_1} \right) \left( \frac{K_{F_A}}{K_{F_A} + S_0} \right) X_1 \]  \hspace{1cm} (5)

\[ r_2 = \mu_2 X_2 = \left( \frac{\mu_2 M'}{K_{SM} + S_2 + \frac{s_2}{K_{SM}}} \right) \left( \frac{K_{F_M}}{K_{F_M} + S_0} \right) X_2 \]  \hspace{1cm} (6)

### Chemical compounds

Several chemical species are included in the model and were obtained from (Bernard et al. 2001)
IC = CO₂ + HCO₃⁻  \quad (7)

\[ K_a = \frac{[H^+] \cdot HCO_3^-}{CO_2} \quad (8) \]

Z = HCO₃⁻ + S₂  \quad (9)

\[ q_M = K_0 \mu_2 X_2 \quad (10) \]

\[ q_c = k_1 a \left( C + S_2 - Z - K_I \left( \frac{\phi - \sqrt{\phi^2 - 4K_IP_f(C + S_2 - Z)}}{2K_IP_f} \right) \right) \quad (11) \]

where \( \phi = CO_2 + K_I P_f + (q_M/k_1 a) \)

\[ pH = -\log \left( \frac{IC + S_2 - Z}{Z - S_2} \right) \quad (12) \]

**Mass balance**

Data from two operation modalities were used to validate the model. Equations 13 and 14 show the mass balance for the fed-batch and batch operation. For the fed-batch operation a constant flow rate of influent was achieved.

\[ \frac{d\xi}{dt} = \frac{F_0}{F_0 t + V_0} (\xi_0 - \xi) + K_i r_i - Q \quad (13) \]

\[ \frac{d\xi}{dt} = K_i r_i - Q \quad (14) \]

**Kinetic parameters**

The following kinetic parameters for the anaerobic population: \( \mu_{1M}, \mu_{2M}, K_{IM}, K_{SA}, \) and \( K_{SM} \) were taken from Bernard et al. (2001), because the same substrate (glucose) was used (In the present study glucose was used as co-substrate). Afterwards, a calibration of these parameters using the experimental data was carried out, from a batch essay with glucose as carbon source. No major changes in these values can be expected since the same substrate was used, despite of the reactor configuration (Batstone et al. 2000a). \( K_0 \) was initially estimated from Vavilin et al. (2008) and calibrated during the dynamic-parameter simulation.

In the present model there are 5 inhibition constants due to the presence of phenol: \( K_{F,H}, K_{F,A} \) and \( K_{F,M} \). However, few studies have determined the inhibition constants of the kinetic of anaerobic phenol degradation (Lin & Lee 2001; Jih et al. 2003; Olguín-Lora & Razo-Flores 2004). Almost all these values were calculated, mainly, for the total anaerobic biomass and not for different population that compose the total anaerobic biomass. These values were considered as initial values for the determination of the final parameter which were used in the model validation. For the parameter determination, experimental data from a batch essay with phenol and glucose as co-substrate (10% and 90% of total COD, respectively) was used. Figure 1 shows the global procedure of the parameter identification and model validation.

**Figure 2** Calibration and identification of kinetic parameters. (a) \( \mu_{1M}, \mu_{2M}, K_{IM}, K_{SA}, \) and \( K_{SM} \) and (b) inhibitions constant. (■) Experimental data; (—) simulation.
Stoichiometric coefficients and physicochemical parameters

All these values were taken from Bernard et al. (2001).

MODEL VALIDATION

Reactor operation and analytical methods

The model was validated by comparison with lab-scale ASBR reactor operation (Donoso-Bravo 2008). Three types of experiments were used for the model validation: Experimental data A: follow-up of the dynamic cycle of operation with 25% of phenol. Experimental data B: the effluent values of the ASBR operation for sequential batches during 50 days of operation using 0, 10, 25, 40% (Phase 1, 2, 3 and 4 respectively) of phenol (glucose completes the 100% of the total COD). Experimental data C: the effluent values of the ASBR operation for sequential fed-batches during 60 days of operation using four concentrations of phenol, as the only carbon source: 0.49, 1.00, 1.05 and 0.95 gCOD/L (Phase 1, 2, 3 and 4 respectively).

During the systems operation samples of influent and effluent were taken, for the following analysis: Chemical oxygen demand (COD) measured by colorimetric method and pH by a specific sensor (APHA 1995), volatile fatty acids (VFA) measured by gas chromatography and phenol concentration by a colorimetric method (Folsom et al. 1990). The biogas flow rate was measured using a mass flow meter.

RESULTS AND DISCUSSION

Parameter calibration

For the parameter calibration the experimental values of the different VFAs measurements were converted in acetic acid equivalents, because the model regards that all VFAs behave as acetic acid ($S_2$). Hence, the concentration values of the

| Initial and calibrated values of kinetic parameters |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Parameter | Initial value | Calibrated value | Unit | Reference |
| $\mu_1M$ | 1.2 | 1.2 | $d^{-1}$ | Bernard et al. (2001) |
| $\mu_2M$ | 0.74 | 0.74 | $d^{-1}$ | Bernard et al. (2001) |
| $K_{IM}$ | 9.28 | 5.0 | mmol/L | Bernard et al. (2001) |
| $K_{SA}$ | 7.1 | 7.1 | g/L | Bernard et al. (2001) |
| $K_{SM}$ | 256 | 125 | mmol/L | Bernard et al. (2001) |
| $K_0$ | 0.99 | 0.86 | d | Vavilin et al. (2008) |
| Inhibition constants | | | | |
| $K_{F,H}$ | 0.06 | 0.0084 | g/L | Olguín-Lora & Razo-Flores (2004) |
| $K_{F,A}$ | 0.06 | 0.84 | g/L | Olguín-Lora & Razo-Flores (2004) |
| $K_{F,M}$ | 0.06 | 0.63 | g/L | Olguín-Lora & Razo-Flores (2004) |
each VFA measured was divided for its molecular weight and then multiplied for the molecular weight of the acetic acid. Finally, the values calculated were added to obtain $S_2$.

Figure 2a shows the simulation and the parameter fit for one reaction cycle without phenol and Table 1 shows the results of the parameter calibration. As was expected, the parameter used in the model properly predicted the performance of the ASBR, since the same substrate were used in both studies. The kinetic parameter of the methanogenic biomass, $K_{SM}$ and $K_{IM}$, decreased close to 50% which is related to the initial value. This can be explained due to the type of seeded sludge which came from an anaerobic filter treating vinasses and had a high specific methanogenic activity according with the substrates characteristics. The biomass presented an adequate affinity for the substrate and a proper ability for VFA degradation. However, the calibrated values of these parameters were fitted to the range of the average reported by Bernard et al. (2001). The hydrolytic constant ($k_0$) was adjusted in value 15% less than the initial one.

Figure 2b presents the fit of the inhibition constants and Table 1 presents the obtained values. According to the no-competitive kinetic considered for the model formulation the hydrolysis process is strongly affected by phenol. This was expected since the initial transformation of the phenol to more readily degradation compounds has been reported as the limiting step. The determined values of the inhibition constants for the acidogenic and methanogenic process were within the range reported by Lin & Lee (2001).

Model validation

To evaluate the quality of the parameter determined and the model application a validation process was carried out

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**Figure 4** | Model validation with experimental data B. (a) tCOD (b) CODphe (c) Biogas (d) pH. (1) 0, (2) 10, (3) 25 and (4) 40% of phenol. (■) Experimental data; (—) simulation.
using different operational conditions. A proper model prediction of a cycle of operation with 25% of phenol was performed compared with the experimental data (Figure 3). A slight deviation occurred at the end of the cycle due to the model, predicted a residual concentration of acetic whereas no VFAs presence was detected. But, it must be pointed out that these values are near the limit of the VFA analysis, therefore such difference probably does not represent a significant deviation. Likewise, the assumptions and simplification as well as the stoichiometric coefficient obtained from the another study may originate some error.

Figure 4 shows the simulation of the main output variables of the anaerobic process, as COD and biogas during the whole study, which were contrasted with the experimental data B (batch modality). The total COD (tCOD) of the effluent was well predicted by the model, for all increases of phenol concentrations in the feeding. However, the model predicted a little lower concentration than the experimental data, which became more significant when the highest phenol concentration was fed. This discrepancy could be due to the concentrations of phenol used, which caused a higher effect on the biomass; perhaps the inhibitory effect caused a toxic effect on the biomass. The same behavior was observed for the COD produced by the phenol (COD_Phenol) (Figure 4b), but at the highest concentration of phenol the difference between the phenol effluent concentration and the tCOD increased, thus an accumulation of VFAs was produced which demonstrates the effect of the biomass activity. This situation is also supported by the biogas simulation (Figure 4c) where there is a greater difference between the simulation and the experimental data which was at the final stages of the operation. A more complex type of inhibition on the methanogenesis is probably exerted by the phenol, but in any case a positive
agreement between the simulation and the experiment was obtained. Throughout the study, the pH simulation was higher than the experimental one. This situation, could have affected the model simulation. Similar deviations were obtained by Bernard et al. (2001) and Batstone et al. (2000b).

Figure 5 shows the model simulation of the effluent variables of the anaerobic process during the operation which contrasted with the experimental data C (fed-batch modality). It is possible to note that a proper fit between both simulated and experimental variables exist. At the beginning of period (3) the simulated values started to move away form the experimental ones, mainly in the tCOD. This situation can be explained due to the washout of biomass that occurred during this part of the operation (Donoso-Bravo 2008) which is a physical phenomena that was not included into the model, and the rise in tCOD was due to the presence of organic suspended solid. The loss of settleability is related to changes in the biomass structure influenced by different variables, for example, by the substrate nature. In the period (4), a toxic effect of the phenol on the anaerobic biomass took place, which produces an increase of residual concentrations of VFAs. The pH was better fitted in this case since a lower difference between simulated and experimental was obtained. Perhaps the fed-batch strategy minimizes the effect of the other alkalinity compounds since a dilution process is carried out during each cycle of operation. Due to the low concentration of phenol in the influent there were unreliable values of the online measurement of the biogas; therefore this variable was not used for the model validation.

CONCLUSIONS

A model with 2 populations and 3 reactions was developed, implemented and validated for the anaerobic treatment of phenol in an Anaerobic Sequencing Batch Reactor (ASBR).

The model predicted the experimental results adequately, which were performed both with a readily biodegradable co-substrate and without a co-substrate.

The theoretical basis of the model is, in general terms, valid, and its utilization to predict the reactors performance is feasible. However, more research is necessary to bear out all the aspects of the model.

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