KINETICS OF SUBSEQUENT PHASES OF THE ANAEROBIC PROCESSES

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ABSTRACT
In the report, kinetics of different phases of anaerobic process was described. The anaerobic process was used for treatment of low concentrated wastewater. The experimental results were compared with the selected theoretical models. While investigating the flock-type sludge structure, the best fit for methanogenesis (the slowest process phase) was found for Monod, Moser, Contois and Teisser models; for granulated sludge the best fit was found for Edwards and Yamne models (inhibition with a substrate was observed). Kinetics of two other phases: acidogenesis and acetogensis followed the Monod, Moser, Contois as well as Chen and Hasimoto models.

KEYWORDS
Anaerobic process, microbial growth, kinetic models, methanogenesis, acidogenesis, acetogenesis

INTRODUCTION

In Polish weather conditions, anaerobic treatment of municipal wastewater may be used mostly for treatment of wastewater with low concentrations of nitrogen and phosphorus as well as for wastewater containing compounds displaying toxicity for activated sludge. Up till now, there is no an explicit comprehensive description of microbial growth within this process.
To fully investigate and describe the kinetics of an anaerobic biodegradation process the experiments were conducted in two types of reactors: a batch reservoir with mixing and a continuous UASB reactor.
Three phases of the anaerobic wastewater treatment process were investigated:

- methanogensis,
- acidogenesis
- acetogensis.

EXPERIMENTAL PROCEDURE

The experimental installation consisted of a tightly closed glass reactor, placed in a thermostat and flushed with nitrogen gas. The reactor diameter was 0,08 m, and its height 0,023 m. The reactor volume was 0,001 m^3. The reactor content was mixed with a magnetic stirrer.
The reactor was fed with anaerobic activated sludge extracted from the UASB reactor. The biomass concentration in the reactor was 26 g dry solids/l and was comparable with the concentration in the UASB reactor.

Biodegradation kinetics of low concentrated wastewater was carried out in two reactors; in both cases a typical research installation was used. A lab - scale UASB reactor was the key element of the experimental stand; the reactor dimensions were:

Table 1. Reactor dimensions.

Reactor	Diameter [m]	Total Hight [m]
I	0.09	1.36
II	0.08	2.50

Both anaerobic reactors were seeded with anaerobic activated sludge taken out from the full-scale UASB reactors, operating at the wastewater treatment plants. The sludge in the laboratory scale reactor I had a floc structure, while the reactor II displayed sludge in a form of granules. The sludge structure was continuously monitored and documented on photographs. A granular form of sludge seems to be the best one and its formation requires specific process conditions. The initial process parameters that favor granulate formation include: initial hydraulic loading, at least 0.3 $m^3/m^3 \cdot h$; pH 6.5–7.8; initial biomass concentration 0.6–25 kg dry solids./m^3; initial COD loading 0.07–0.49 kg COD/kg dry solids.·h; A granules formation time is rather long (up to couple of months) and influenced by reactor operating temperatures. Microbiological composition of sludge depends on type of substrate rather then sludge structure (Singh et al. 1999).
To assure stability and consistency of the process parameters throughout the operating cycle, the synthetic wastewaters were used in the experiments.
During the course of experiments, the following parameters were changed:

- actual retention time in the reactor,
- influent wastewater concentration,
- temperature: 25 °C, 30°C, and 35 °C.

In each series of experiments only one parameter (the actual retention time in the reactor) varied. The other parameters such as the COD influent concentration and temperature remained constant.
During the experiments the following process parameters were analysed (according to the Polish Standards):

- pH in the influent and effluent (determined with the accuracy down to 0.01 (PN-72/C-04540/01)
- temperature inside the reactor,
- COD in the reactor influent and effluent (PN-74/C-04578.03 and 5220B, see Standard Methods 17th 1989),
- biomass concentration at different reactor levels and in the effluent (PN-72/C-04559.02),
- biogas content (gas chromatography),
- carboxylic acids (VFA) concentration in the influent and effluent (gas chromatography) (Kryłów i Lach 1998)

In addition, the basic rheological parameters of the anaerobic activated sludge were determined using reoviscometer HAAKE RS 75.
To estimate the reaction kinetics, the experimental data were plotted as a relationship between the specific growth rate and a substrate concentration. Anaerobic biodegradation was carried out in the UASB reactor.

DISCUSSION OF THE RESULTS

An anaerobic process of substrate transformation may be described using a theory of a continuous microorganisms growth and its kinetics. Since anaerobic biodegradation of wastewater incorporates numerous steps, the process itself may also be illustrated as successive sequence of steps, limiting each of the substrate degradation steps (Malina and Pohland 1992).

The kinetic models, analyzed the paper, included also microorganisms decay e.g.:

$$\mu = \mu_{\max} \cdot \frac{C_S}{K_S + C_S} - b \tag{1}$$

where: b – specific decay rate

Microorganisms decay results from accumulation of toxic metabolism by-products in medium

In the paper, the specific microbial growth rates were calculated for methanogenesis, acetogenesis and a glucose biodegradation process.

Methanogenesis can be described with the reaction:

$$CH_3COOH + CH_{1.79}O_{0.5} \rightarrow 0.02CH_{1.79}O_5 + 0{,}94CH_4 + 0{,}94CO_2 \tag{2}$$

The empirical expression used for microbial cell $CH_{1.79}O_5$ was assumed after Roelsem (Szewczyk 1993).

During the first approximation, the parameters obtained in the experiments were assumed in the Monod equation and then compared with 20 theoretical models. The best fit of the experimental biodegradation curves (for experiments conducted in the reactor with floc sludge) was observed for the Monod, Moser, Teisser, Conti and Chen and Hashimoto models (Figures 1 and 2). The average errors observed between the model curve and the experimental curve are shown in Table .2.

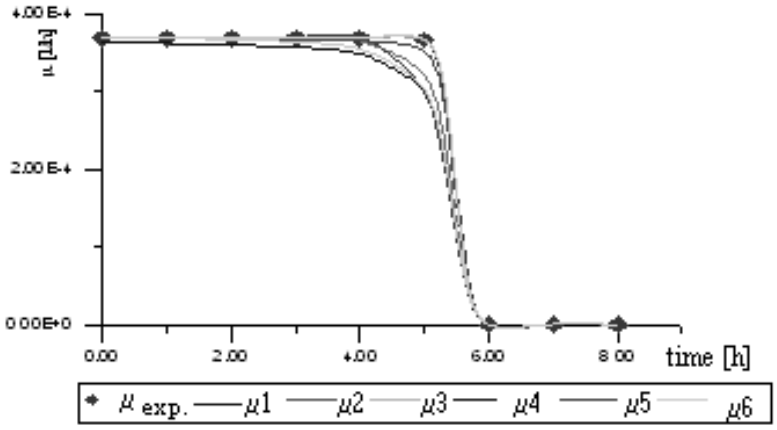

Figure 1. Microorganisms growth versus time for different kinetic models (methanogensis, floc sludge, temperature 35°C)

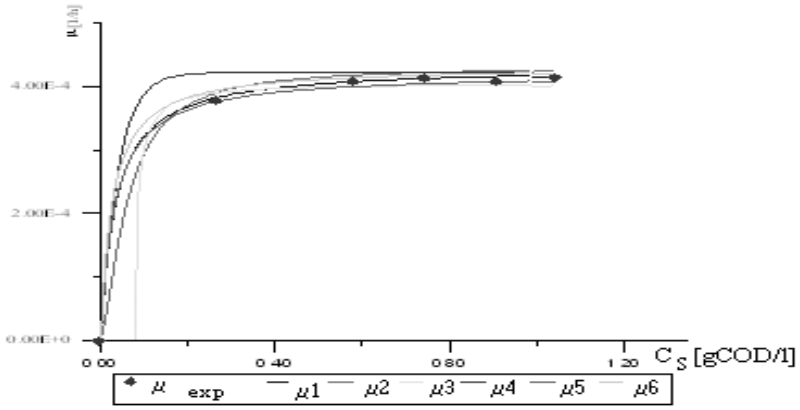

Figure 2. Microorganisms growth versus time for different kinetic models (methanogensis, floc sludge, temperature 35°C)

Table 2. The average errors in the fitted growth models for the UASB reactor (floc sludge).

Model	Symbol	The average error
Monod	μ1	3.35%
Moser	μ2	1.44 %
Moser (revised)	μ3	0.12 %
Teissier	μ4	1.67%
Contois	μ5	0.65%
Chen and Hashimito	μ6	2.29%

The best fit for the experimental biodegradation curves, obtained in a reactor with granulated sludge, was found for the Andrews, Edwards, Webb and Yamane models (Figures 3 and 4.). The average errors calculated for the experimental and the model curves are shown in Table 3.

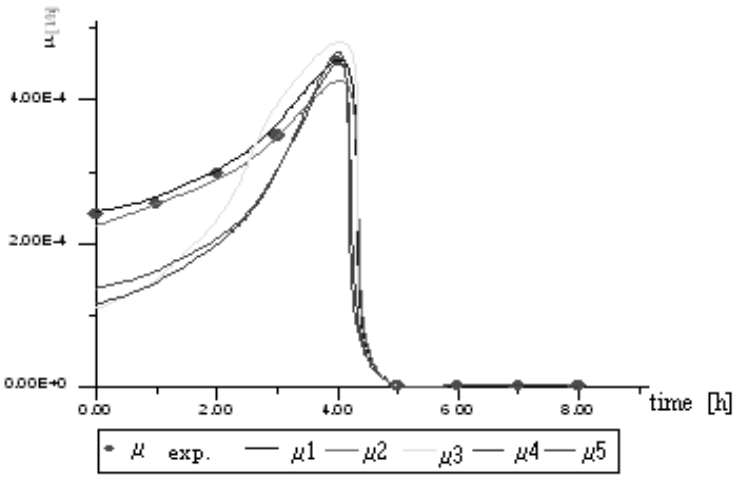

Figure 3. Microorganisms growth versus time for different kinetic models. (methanogensis, granulate sludge, temperature 35°C)

Table 3. The average errors in the fitted growth models for the UASB reactor (granulated sludge).

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Webb	μ3	0.12 %
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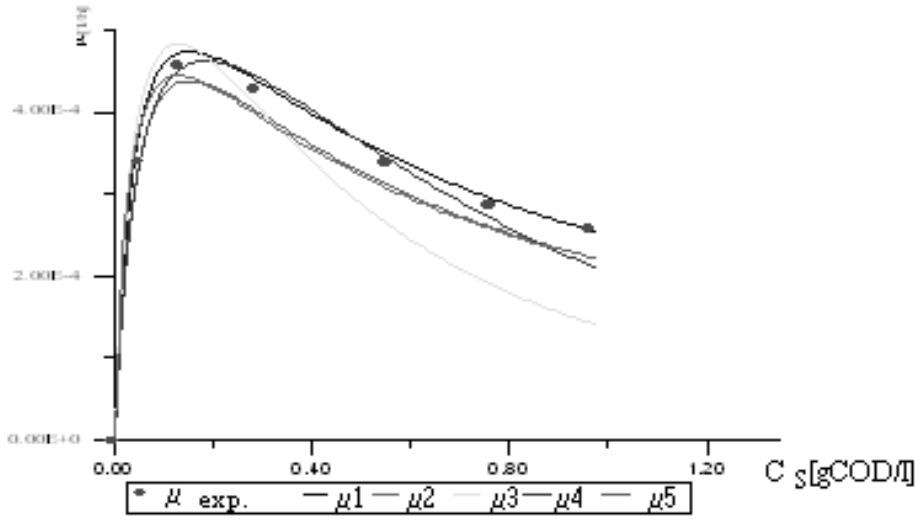

Figure 4. Microorganisms growth versus substrate concentrate for different kinetic models (methanogensis, granulate sludge, temperature 35°C)

The best fit for the methanogenesis process in the UASB reactor with floc sludge was obtained for the classic and revised Moser models. The kinetic experiments were conducted at a very high biomass concentration, about 26 g dry solids./dm^3. Therefore, it seems reasonable to use the Contios model for this process description; this model takes into account the impact of biomass concentration on microbial growth.
For the reactor with granulated sludge the best fit of the experimental curve was observed for the Edwards and Andrews models.
Acetogenesis is described by the following reactions:

$$CH_3CH_2COOH + C_6H_{12}O_6 \rightarrow 0{,}025C_6H_{12}O_6 + 1{,}18CH_4 + 1{,}67CO_2 \quad (3)$$

$$CH_3CH_2CH_2COOH + C_6H_{12}O_6 \rightarrow 0{,}03C_6H_{12}O_6 + 1{,}41CH_4 + 2{,}41CO_2 \quad (4)$$

The experimental results (from the series with a mixture of propionic and butyric acids, as a substrate) were compared with 20 theoretical models.
During acetogenesis, degradation of propionic and butyric acids to methane goes through an intermediate stage where acidic acid is produced. In such case, the overall Monod equation can be expressed as:

$$\mu = \left(\mu_{,\max 1} \cdot \frac{C_{S1}}{K_{S1} + C_{S1}} - b_1 + \mu_{\max 2} \frac{C_{S2}}{K_{S2} + C_{S2}} - b2 \right) \quad (5)$$

The best fit was obtained for the Monod, Teisser and Grau, Conti and Chen and Hashimoto models (Figures 5 and 6). The average errors, calculated for the experimental and model curves of microbial growth, are shown in Table 4.

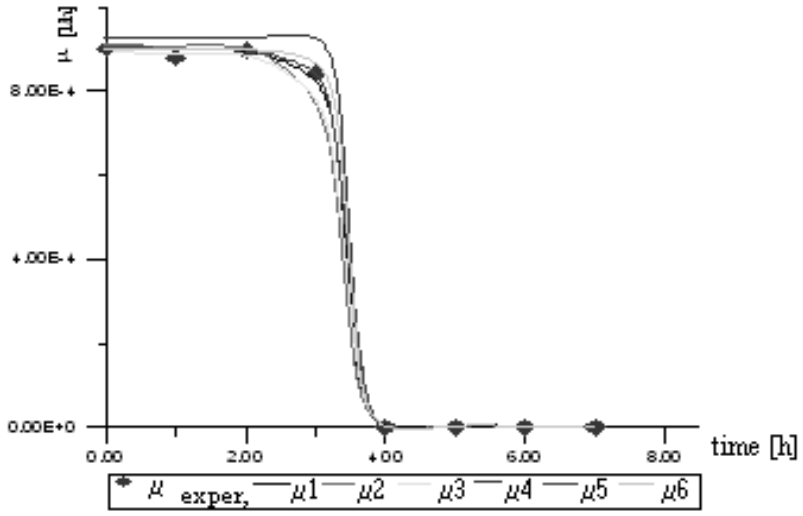

Figure 5. Microorganisms growth versus time for different kinetic models. (methanogensis, granulate sludge, temperature 35°C)

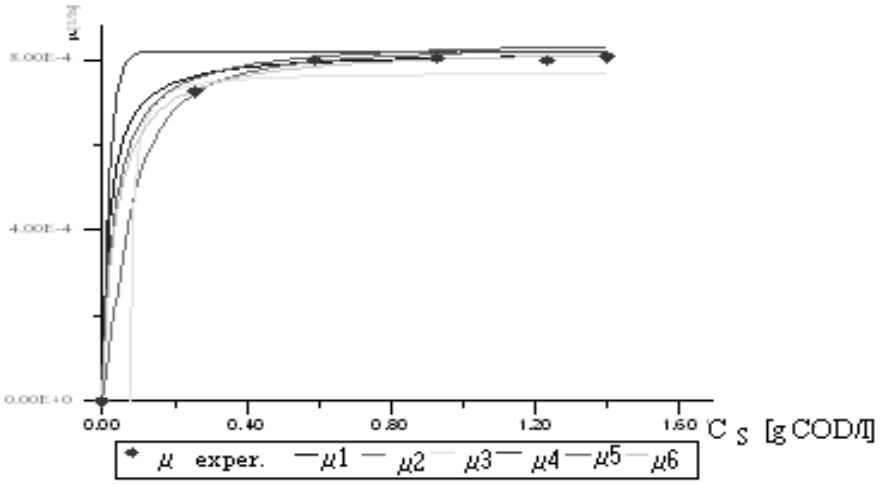

Figure 6. Microorganisms growth versus substrate concentrate for different kinetic models (methanogensis, granulate sludge, temperature 35°C

Table 4. The average errors in the fitted microbial growth models.

Model	Symbol	Average error	
		Flocs	Granules
Monod	μ1	2.76%	2.05%
Moser	μ2	10.58 %	9.5%
Moser (revised)	μ3	1.47%	2.8 %
Teissier	μ4	1.6%	3.25
Contois	μ5	1.15%	2.05%
Chen and Hasimito	μ6	5.02%	4.6%

The best fit for acetogenesis was obtained for the Contois' model; it confirms that the last stages of biodegradation process are limited with biomass concentration.
Degradation of glucose can be described with the set of the following reactions:

$$2C_6H_{12}O_6 \rightarrow 2CH_3CH_2CH_2COOH + CH_4 + 3CO_2 + H_2O \quad (7)$$

$$2CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 3CH_4 + CO_2 \quad (8)$$

$$2CH_3COOH \rightarrow 2CH_4 + 2CO_2 \quad (9)$$

$$2C_6H_{12}O_6 \rightarrow 6CH_4 + 6CO_2 \quad (10)$$

The results from the experimental series, with a mixture of propionic and butyric acid as a substrate, were compared with 20 theoretical models.
Breakdown of glucose to methane gas proceeds as a two-stage process. In the first intermediate stage, propionic and butyric acids are produced, while in the second intermediate stage acetic acid is produced. In this case, the general Monod equation can be expressed as:

$$\mu = \left(\mu_{,\max 1} \cdot \frac{C_{S1}}{K_{S1} + C_{S1}} - b_1\right) + \left(\mu_{\max 2} \frac{C_{S2}}{K_{S2} + C_{S2}} - b_2\right) + \left(+\mu_{\max 3} \frac{C_{S3}}{K_{S3} + C_{S3}} - b_3\right) \quad (11)$$

The best fit was obtained for the Monod, Teisser and Grau, Conti and Chen and Hashimoto models (Figures 7 and 8). The average errors, calculated for the experimental and model curves of microbial growth, are shown in Table 5.

Table 5. The average errors in the fitted microbial growth models.

Model	Symbol	Average error	
		Flocs	Granules
Monod	μ1	2.06%	1.98%
Moser	μ2	11.58 %	12.45%
Mosera (revised)	μ3	4.8 %	4.02%
Liveawer - Burk	μ4	2.6%	8.5%
Contois	μ5	2.5%	2.32%
Chen and Hasimito	μ6	1.2%	1.4%

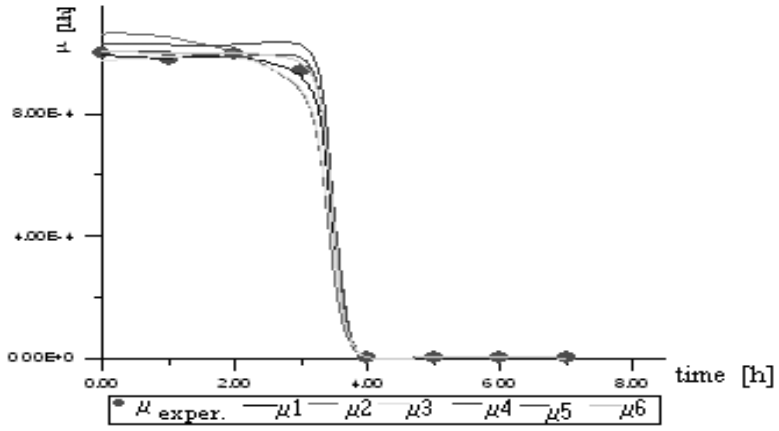

Figure 7. Microorganisms growth versus time for different kinetic models (acetogensis, floc sludge, temperature 35°C)

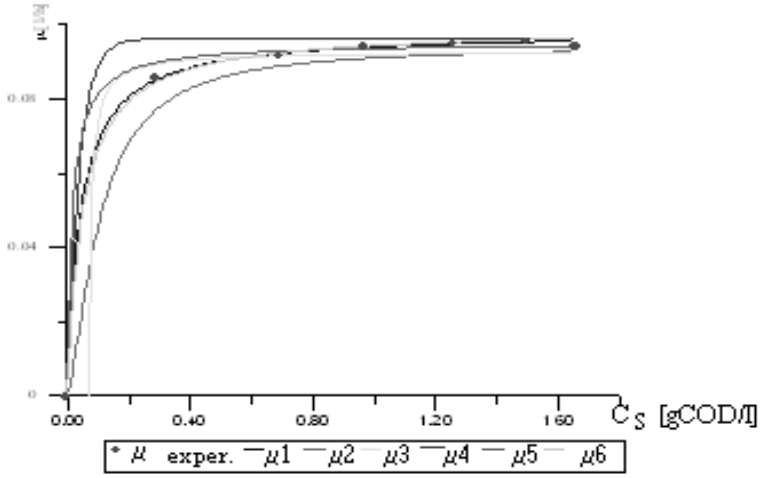

Figure 8. Microorganisms growth versus substrate concentration for different kinetic models (acetogensis, floc sludge, temperature 35°C)

Based on the extended analysis, as the simplest solution, the Monod model was proposed for a design of reactors with floc sludge; for reactors with granulated sludge matanogenesis is described in the best way by the Andrews model. A detailed description of biodegradation kinetic model was presented. For the Monod model, the kinetic parameters for different temperatures and staged of digestion were developed both in analytical and graphical ways.

SUMMARY

Based on the experimental results of the biodegradation kinetics the following conclusion can be formulated:

1. The Monod kinetics is a convenient tool to describe the individual stages of the anaerobic digestion process.
2. The structure of anaerobic activated sludge had no impact on the type of kinetic description of glucose breakdown (acidogenesis) to lower carboxylic acids (propionic and butyric acids) as well as their breakdown to acetic acid (acetogenesis). These anaerobic digestion reactions can

be most accurately described by the kinetic formulas of Monod, Contois as well as Chen and Hashimoto.

3. Description of the last stage of anaerobic digestion i.e. methanogenesis of low concentrated wastewater is influenced by the activated sludge structure. During conversion of acidic acid to methane in the UASB reactor with granulated sludge and inhibitory effect can be observed. Inhibition is caused by substrate (undisociated acidic acid) and can be described with Andrews or Edwards kinetics.
4. Methanogenesis in the UASB reaktor with floc sludge proceeds without an inhibitor. The process is most accurately described by Contois, Monod, Chen and Hashimoto or Moser equations, with the error less then10% .
5. Biodegradation of low concentrated wastewater proceess faster in a reactor with granulated sludge.
6. While modeling and designing the process of municipal wastewater degradation in the UASB reactors with granulated sludge, an inhibition with substrate during methanogenesis has to be considered; the process can be described with the Andrews equation.
7. While modeling and designing the process of low concentrated wastewater biodegradation in the UASB reactors with floc sludge, kinetics of consecutive steps of metanogenesis may be described with Monod or Chen and Hashimoto models.

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