KINETICS OF ANAEROBIC PROCESSES

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ABSTRACT
In the paper, description of anaerobic treatment of municipal wastewater, according to the proposed kinetic model, has been presented. The experimental results of microbial growth predictions showed the greatest resemblance to the models of Monod, Teisser, Contois as well as Chen and Hashimoto.

KEYWORDS
Anaerobic biodegradation, kinetics model, methanogenesis, acetogenesis, acidogenesis.

INTRODUCTION
During the research, the author focused on anaerobic treatment of municipal wastewater. So far, this subject as well as a complete description of microbial growth kinetics, have not been thoroughly investigated.
To fully understand and describe the kinetics of anaerobic biodegradation process the experiments were conducted in continuos flow reactor:
Three phases of the anaerobic wastewater treatment process were investigated:
- metanogensis,
- acetogenesis
- acidogensis.

EXPERIMENTAL PROCEDURE
The experimental installation consisted of a glass reactor placed in a thermostat 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.

The anaerobic reactor was 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 had a floc structure.

To assure the stability and consistency of the process parameters, throughout the operating cycle, the synthetic wastewater 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, 35 °C.

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

- pH of the influent and effluent (determined with the accuracy down to 0.01 (PN-72/C-04540/01)
- temperature inside the reactor,
- COD in the influent and effluent to the reactor (PN-74/C-04578.03 oraz 5220B wg Standard Methods 17th 1989),
- biomass concentration at different reactor levels and in the effluent (metodą wagową wg PN-72/C-04559.02),
- biogas content (gas chromatography),
- content of carboxylic acids (VFA) 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 reowiskozymeter HAAKE RS 75.

PROCESS KINETIC MODEL

The model can accommodate the successive phases of the anaerobic reaction and describe the following mechanism:

$$X_1 + S \xrightarrow{k_1} b \cdot P_1 + n \cdot X_1 \quad (1)$$

$$X_2 + P_1 \xrightarrow{k_2} d \cdot P_2 + m \cdot X_2 \quad (2)$$

$$\ldots$$

$$X_n + P_{n-1} \xrightarrow{k_n} u \cdot P_n + z \cdot X_n \quad (3)$$

where : X - biomass,
S - substrate,
P - product

Based on the above relationships the microbial growth for the entire process can be described as:

$$\mu_C = \frac{dC_X}{C_X \cdot dt}, \quad (4)$$

where: $C_X = C_{X1} + C_{X2} + ... + C_{Xn}$. (5)

It was assumed that the fraction of the particular types of microorganisms in the biomass remains constant. Therefore, a set of kinetic equations can be written as:

$$-\frac{dC_S}{dt} = \mu_1(C_S)\cdot C_{X1} = r_1 \tag{6}$$

$$\frac{dC_{P_1}}{dt} = Y_{P_1X}\cdot\mu_1\cdot(C_S)\cdot C_{X_1} = Y_{P_1X}\cdot r1 \tag{7}$$

$$\ldots$$

$$\frac{dC_{P_n}}{dt} = Y_{P_nX}\cdot\mu_n\left(C_{P_{n-1}}\right)\cdot C_{X_n} \tag{8}$$

$$r_1 = r_2 = \text{K} = r_n = f(C_S) \tag{9}$$

A mass balance for the individual intermediate product in this system can be expressed as:

$$\frac{dC_{P,n}}{dt} = Y_{P_n,X}\cdot\mu_n\left(C_{P,n-1}\right)\cdot C_{X_n} - \frac{\mu_{n+1}\left(C_{P,n}\right)}{Y_{X,P_n}}\cdot C_{X_{n+1}} \tag{10}$$

An increase of a concentration of those particular microorganisms, which participate in each phases of the process is very difficult to measure and therefore the following relationships have been assumed:

$$C_{X_1} = \varphi_1\cdot C_X \tag{11}$$

$$C_{X_1} = \varphi_2\cdot C_X \tag{12}$$

$$\ldots$$

$$C_{X_n} = \varphi_n\cdot C_X, \tag{13}$$

where: φ_1, φ_2, ..., φ_n – mass fraction of biomass elements.

Substituting equations (11) – (13) in equation (4) and rearranging the latter, the following relationship can be obtained:

$$\mu_C = \mu_1\cdot\varphi_1 + \mu_2\cdot\varphi_2 + \text{K} + \mu_n\cdot\varphi_n. \tag{14}$$

The relationship describes the overall microbial growth rate of the process as the sum of the bacterial growths observed during each individual stage of the process.

$$\mu_C = \sum_{i=1}^{n}\mu_i\cdot\varphi_i, \tag{15}$$

where: μ_i – specific microbial growth rate in a single individual stage of the process.

If the microorganism growth in each individual stage follows the Monod's kinetics then the overall specific microbial growth rate can be expressed as:

$$\mu_C = \sum_{i=1}^{n}\left(\varphi_i\cdot\left(\mu_{\max_i}\cdot\frac{C_{S_i}}{K_{S_i}+C_{S_i}}\right)\right). \tag{16}$$

To verify the mechanism assumed for anaerobic biodegradation of wastewater, the mechanism of VFA conversion to methane, with acetic acid as an intermediate product, was investigated. Based on the assumed mechanism, the following set of equations was obtained, each one describing the rate of the particular reaction:

$$\frac{dC_X}{dt} = Y_{XS} \cdot k_1 \cdot C_S \cdot C_X + Y_{XP_p} \cdot k_2 \cdot C_{P_p} \cdot C_X \quad (17)$$

$$\frac{dC_S}{dt} = -k_1 \cdot C_S \cdot C_X \quad (18)$$

$$\frac{dC_{P_p}}{dt} = -k_2 \cdot C_X \cdot C_{P_p} \quad (19)$$

$$\frac{dC_{P_k}}{dt} = Y_{P_k P_p} \cdot k_2 \cdot C_{P_p} \cdot C_X + Y_{P_k S} \cdot k_1 \cdot C_S \cdot C_X \quad (20)$$

As the initial values C_{S0}, C_{Pp0}, $C_{Pk0,}C_{X0}$, the values obtained during the experiments were assumed. The experimental values fitted a simulation curve with an error lower then 15%. Hence, it can be stated that the proposed mechanism of substrate biodegradation and intermediate products generation is correct (Fig. 1,2, 3, 4).

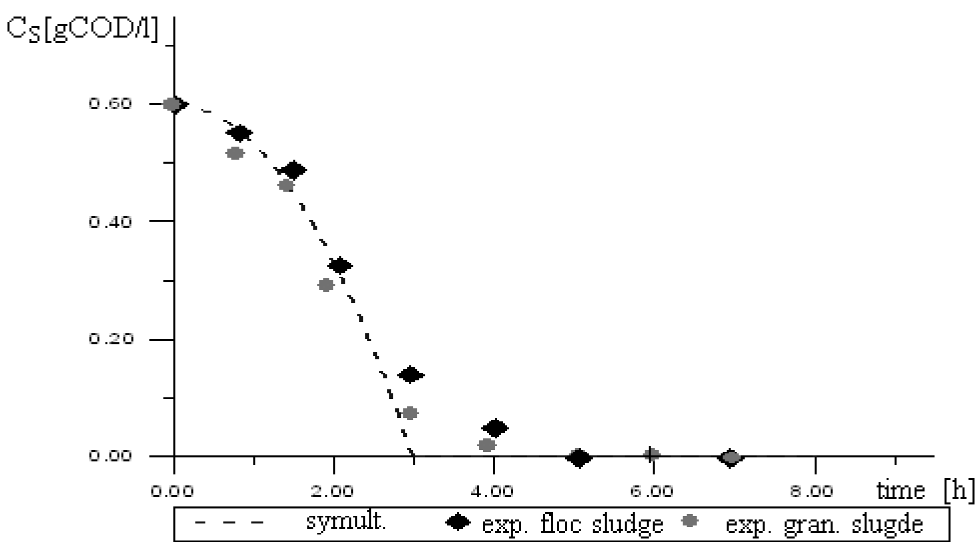

Figure.1. Substrate concentration versus time

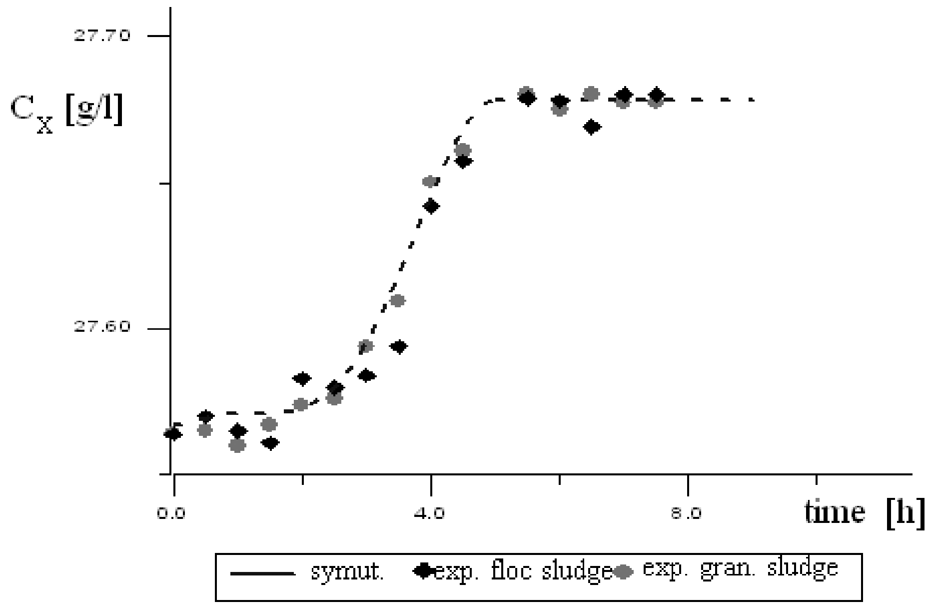

Figure 2. Biomass concentration versus time

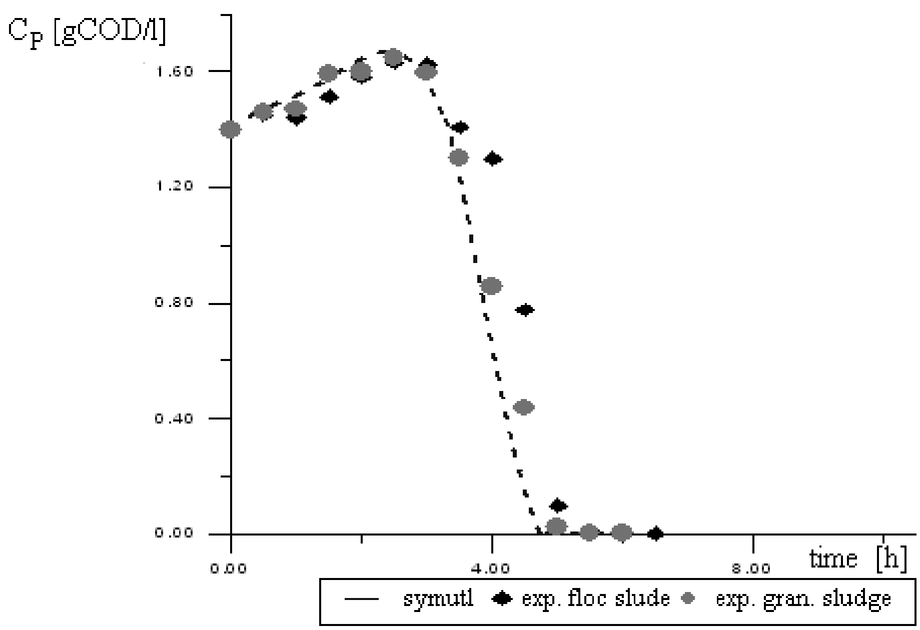

Figure 3. Intermediate product concentration versus time

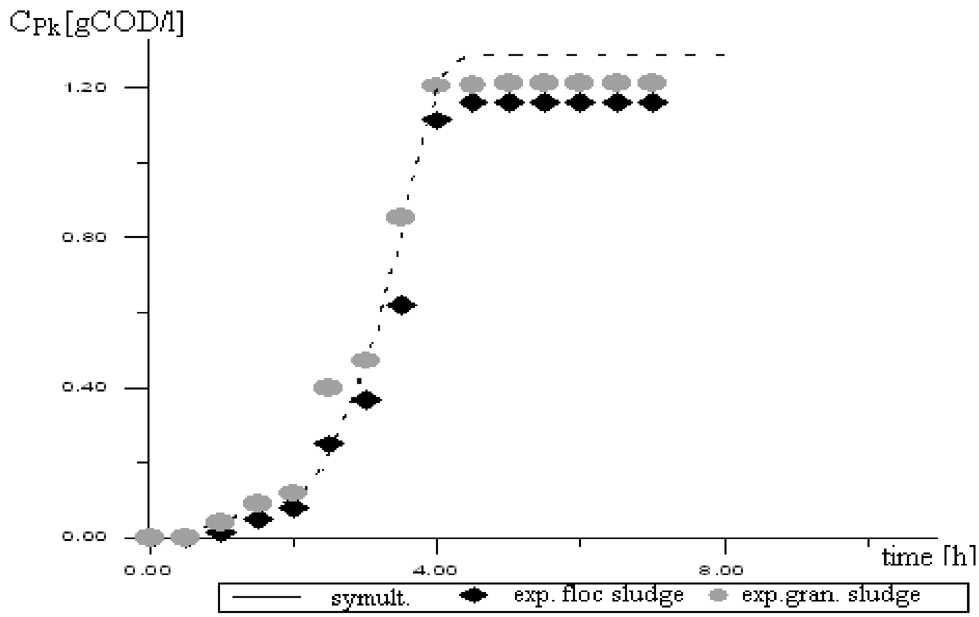

Figure 4. Final product concentration versus time

To estimate the values of the kinetic parameters the experimental results were compared with different kinetic models. The best fit was obtained for the Monod, Teisser Contois as well as Chen and Hashimoto models (error less then 10%).

The following example of biodegradation of glucose can serve as an illustration of application of the proposed model of microbial growth in anaerobic wastewater treatment.
Typical conversion of glucose can be described with the set of the following reactions:

$$2C_6H_{12}O_6 \rightarrow 2CH_3CH_2CH_2COOH + CH_4 + 3CO_2 + H_2O \quad (21)$$

$$2CH_3CH_2CH_2COOH + H_2O \rightarrow 5CH_4 + 3CO_2 \quad (22)$$

$$2C_6H_{12}O_6 \rightarrow 6CH_4 + 6CO_2 \quad (23)$$

The results from the experimental series, with a mixture of propionic and butyric acid as a substrate, were compared with the 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's equation can be expressed as:

$$\mu = \left[\varphi_1 \cdot \left(\mu_{max1} \cdot \frac{C_{S1}}{K_{S1}+C_{S1}} - b_1 \right) + \varphi_2 \cdot \left(\mu_{max2} \frac{C_{S2}}{K_{S2}+C_{S2}} - b_2 \right) + \varphi_3 \cdot \left(+ \mu_{max3} \frac{C_{S3}}{K_{S3}+C_{S3}} - b_3 \right) \right] \quad (24)$$

The paper presents a kinetic model of anaerobic wastewater biodegradation. Following the Monod's kinetics, the kinetic parameters were determined both in graphical and analytical way. The parameters were determined for different temperatures (25°C, 30°C, 35°C) and for different stages of the anaerobic digestion process. The results are presented in Tables 1.

Table 1. Kinetic parameters of the Monod's equation for low strength wastewater.

Substrate	Process	Temp. °C	Sludge	Y_{XS} [g SS. / gCOD]	K_S [gCOD /dm^3]	μ_{max} [1/h]	b [1/h]	q_P [m^{3}CH$_4$/ gCOD$_{rem}$]	q_{smax} [gCOD/ g SS.·h]
Acetic acid	Methanogenesis	25	floc	0.044	0.0175	0.0003	0.00001	0.15	0.146
VFA (without acetic acid)	Acetogenesis	25	floc	0.46	0.0192	0.00043	0.00001	0.16	0.026
Hydrocarbons (glucose)	Acidogenesis	25	floc	0.05	0.25	0.073	0.001	0.165	0.194
Acetic acid	Methanogenesis	25	granules	0.044	0.02	0.0008	0.00001	0.17	0.16
VFA (without acetic acid)	Acetogenesis	25	granules	0.046	0.034	0.0096	0.00001	0.182	0.0287
Hydrocarbons (glucose)	Acidogenesis	25	granules	0.05	0.125	0.08	0.001	0.188	0.212
Acetic acid	Methanogenesis	30	floc	0.045	0.01	0.00038	0.0001	0.165	0.012
VFA (without acetic acid)	Acetogenesis	30	floc	0.047	0.02	0.00057	0.0001	0.17	0.015
Hydrocarbons (glucose)	Acidogenesis	30	floc	0.044	0.25	0.0741	0.001	0175	0.03
Acetic acid	Methanogenesis	30	granules	0.045	0.01	0.00038	0.0001	0,165	0.012
VFA (without acetic acid)	Acetogenesis	30	granules	0.047	0.02	0.00057	0.0001	0.17	0.015
Hydrocarbons (glucose)	Acidogenesis	30	granules	0.044	0.25	0.0741	0.001	0.175	0.03
Acetic acid	Methanogenesis	35	floc	0.054	0.035	0.00045	0.00001	0.172	0.0317
VFA (without acetic acid)	Acetogenesis	35	floc	0.047	0.023	0.00063	0.00001	0.179	0.039
Hydrocarbons (glucose)	Acidogenesis	35	floc	0.055	0.25	0.0004	0.001	0.185	0.338
Acetic acid	Methanogenesis	35	granules	0.054	0.31	0.00085	0.00001	0.176	0.07
VFA (without acetic acid)	Acetogenesis	35	granules	0.047	0.0375	0.0001	0.00001	0.183	0.039
Hydrocarbons (glucose)	Acidogenesis	35	granules	0.055	0.35	0.084	0.001	0.196	0.352

SUMMARY

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

1. The Monod's kinetics is convenient to describe the individual stages of the 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.

In the process design and modeling, kinetics of different stages of anaerobic biodegradation of low strength wastewater, in reactors with sludge flocs, can be illustrated with the equations of Monod or Chen and Hashimoto.

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