

# COMPUTER SIMULATION OF VFA GENERATION WITH THE ANALYSIS OF KINETIC, TECHNOLOGICAL AND TECHNICAL PARAMETERS

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## ABSTRACT

Generation of VFAs from primary sludge is a part of technological optimization of biological phosphorus removal, sometimes also nitrogen removal. Introduction of new regulations in Poland enforcing nitrogen and phosphorus effluent standards depending on a size of WWTP, makes VFAs generation process more important, especially for medium and large WWTPs.

This paper presents results of application of DSP simulation program for VFAs generation process in two Polish WWTPs using different types of pre-fermenters: complete mix and static in side-line of sludge stream. Kinetic factors for mathematical model were determined in batch tests, then simulations of full-scale processes were carried out. Results were compared to operational data. Some technological and technical factors affecting the processes were analyzed and conclusions regarding their optimization were given.

## KEYWORDS

Mathematical modelling, phosphorus removal, pre-fermenter, VFAs generation

## INTRODUCTION

The pre-fermentation of sludges to generate volatile fatty acids (VFAs) enhancing biological nutrients removal from the wastewater, is more and more often applied in new wastewater treatment plants (WWTPs) and also used for upgrading the old ones. However, these actions do not always improve phosphorus removal and even then additional chemical precipitation must be used. The reason for pre-fermenters ineffectiveness is the deficiency in the design methods. There is a lack of precise guidelines and methodology of pre-design investigations that would give the designers the correct answer regarding the optimizing of VFAs generation. There is not sufficient knowledge concerning an installation that produces VFAs most effectively and would be best suited for the particular type of wastewater. Finally, the process engineer should be informed about the parameters, which provide the best solution for optimal plant operation. In recent times the pre-fermenters design was based mostly on the very general and vague guidelines and thus more on the designers intuition than on solid data. The local specifics were not considered and the lack of precisely defined rules of operation causes the WWTPs operators to abandon any control of operational parameters.

The full analysis of the biological VFA generation involves recognizing the kinetics of the process and determining kinetic constants, which is a very complex problem. Dr Elisabeth v. Munch (Science Traveller International, Australia) tried to solve this problem by creating the computer

simulation program “Dynamic Simulator for Prefermenters (DSP)”. With this program – applying kinetic constants assumed by the authors – it is possible to optimise the process of pre-fermentation. As the assumption of identical kinetic constants for all sorts of sludge is an over-simplification, it is essential to determine them for a given sludge, which would lead to the proper model calibration. Consequently, based on the new established values of kinetic constants, it would be possible to provide more effective technical design of the prefermenter.

In this paper we want to show the results of our study and calculations estimating the kinetic constants for a primary sludge pre-fermentation, for two Polish WWTPs that exploit such process. These results and the operational data from the WWTPs helped to assess the effectiveness of the existing prefermenters and draw some initial conclusions regarding the optimal solution for the pre-fermentation processes.

### MODEL DESCRIPTION

Mathematical model of VFA generation is usually treated as a part of a more general process - methane fermentation. In this classical simplifying approach two stages are distinguished: hydrolysis of large molecules and subsequent VFAs generation by acidogenic bacteria (Eastman and Ferguson, 1981; Henze et al., 2002). Kinetics of hydrolysis is described as first-order, with rate proportional to substrate concentration, sometimes including saturation effect of biomass with maximal hydrolytic capacity (Henze et al., 2002). There is no distinction between different types of substrates - all hydrolysable substances are regarded as one substrate, expressed in terms of COD. VFAs generation from hydrolysis products is described by Monod kinetics, with bacterial growth and then decay of fermenting microorganisms.

Such a model is too general to include all the phenomena and factors affecting VFA generation. As such, it cannot be effectively used to optimise the design and operation of prefermenters. Münch et al. (1999a) developed a more complicated model aimed specifically at this purpose. Kinetics of this model was a modified version of the Negri et al. (1993) model, proposed originally for VFAs generation from organic fraction of municipal waste. While trying to reflect biological processes more accurately, this model is still a compromise with its practical usability. It is noticeable, that the authors intention was to base its calibration on relatively easy available analyses like COD (soluble or insoluble), Kiejdahl and ammonia nitrogen and VFAs concentration.

In this model hydrolyzable substrates are divided into insoluble (particulate) organics (concentration  $C_{is}$ , expressed as COD), soluble organics  $C_s$  and organic nitrogen contained in proteins  $C_{prot}$ . Both insoluble and soluble substrates are converted into monomer species  $C_{mo}$ , nitrogen is hydrolyzed into ammonia nitrogen  $C_{NH4-N}$ . Hydrolysis of insoluble organic matter proceeds with the rate described by the following expression, with Contois-like inhibition by biomass growth:

$$r_{h,is} = k_{h,is} \frac{C_{is} C_e}{C_{Xa}} \quad (1)$$

where  $C_e$  describes concentration of hydrolytic enzymes and  $C_{Xa}$  concentration of acidogenic biomass. Soluble macromolecules are hydrolyzed according to the second-order equation:

$$r_{h,s} = k_{h,s} C_s C_e \quad (2)$$

Both processes are linked to hydrolytic enzyme production via the yield coefficient  $Y_e$ . Enzymes undergo simultaneous denaturation:  $r_{d,e} = d_e C_e$ . Rate of ammonification of proteins is described by

an expression similar to that used for hydrolysis of insoluble substrates, with ammonia nitrogen as product:

$$r_{amm} = k_{amm} \frac{C_{prot} C_e}{C_{Xa}} \quad (3)$$

Soluble monomer species are next used by acidogenic bacteria for their growth which is associated with VFA generation. Microorganisms use also ammonia nitrogen to build their biomass with the growth rate:

$$r_{Xa} = \mu_{max,a} \frac{C_{mo}}{K_a + C_{mo}} \cdot \frac{C_{NH4-N}}{K_n + C_{NH4-N}} C_{Xa} \quad (4)$$

No distinction is made between different VFAs and all they are described as VFA-COD ( $C_{VFA}$ ). VFA are utilized by methanogenic bacteria for growth and methane production. Their growth rate is also described by Monod kinetics:

$$r_{Xm} = \mu_{max,m} \frac{C_{VFA}}{K_m + C_{VFA}} \cdot \frac{C_{NH4-N}}{K_n + C_{NH4-N}} C_{Xm} \quad (5)$$

Both types of microorganisms undergo decay:  $r_{d,a} = d_a C_{Xa}$  (6) and  $r_{d,m} = d_m C_{Xm}$  (7). Upon their death nitrogen from biomass is released as protein nitrogen, while organic matter (together with denaturated enzymes) comes back to the pool of soluble hydrolyzable substrate.

As mentioned above, calibration of this model relies on simple analyses: COD, Kiejdahl and ammonia nitrogen, and VFAs. It is assumed that soluble COD comprises of soluble substrate, monomer species, VFAs and hydrolytic enzymes. Total COD includes soluble COD plus insoluble substate and both types of bacteria: acidogenic and methanogenic. Total Kiejdahl nitrogen is a sum of protein nitrogen, ammonia nitrgen and nitrogen in bacterial biomass.

Münch et al. (1999a) used the above kinetic model for dynamic modelling of prefermenters. However, to make its use more practicable, there are many simplifications made. There is no consideration of reactor hydraulics and all configurations of prefermenters are reflected by applying different values of HRT and SRT. For the majority of coefficients constant values are assumed from the literature and model calibration is in fact an estimation of three factors only – hydrolysis constants  $k_{h, is}$ ,  $k_{h, s}$ ,  $k_{amm}$ . Because of difficult measurement, initial concentrations of acidogenic and methanogenic bacteria are typically assumed as constant fractions of insoluble COD, similarly hydrolytic enzymes at the time zero comprise assumed fraction of soluble COD diminished by VFA-COD.

This model was verified on the base of literature data (Münch et al., 1999a), some data from full-scale prefermenters and dynamic experiment (Münch et al., 1999b). The results can be regarded as fairly good.

DSP simulation software (Science Traveller International) makes use of the above model. It also includes some additional features: pH prediction on the base of VFA concentration in prefermenter, according to method developed by Münch and Greenfield (1998), and option for including temperature effect. However, this latter part has been not yet validated experimentally.

Assessing the practical value of the model, it should be stated that in spite of many remarkable simplifications and shortcomings it is a certain step forward in prefermenter technology. It makes an attempt to give more rationally justified background to prefermenter performance optimization, instead of so far applied empirical and intuitive methods. What is more, it requires relatively easy available analytical data, in contrast to quite sophisticated measurements necessary for other more complicated models.

## **MATERIALS AND METHODS**

### **Batch tests**

Determination of kinetic constants of the pre-fermentation process were carried out in batch tests with the primary sludge from the Jaworzno and Jaslo WWTPs. The prefermenters in these WWTPs were operated in different configurations, described below.

Primary sludge for these tests was taken from the influent channel by pumping raw wastewater to the model clarifier, where sludge was separated and successively removed from a hooper to a collective vessel. The amount of the sludge needed for the tests was about 1 l and its collection time was no longer than 1.5 hour. The sludge was taken directly from the influent because the previous research showed that VFAs production begins immediately in the primary clarifier.

The collected sludge, after thorough mixing, was poured into 8 150 ml dark glass bottles. The bottles were capped with rubber caps leaving gas escape through plastic pipes, with water close. At the beginning the samples were flushed with nitrogen to remove oxygen and other gases. Magnetic rods were placed in the bottles and the mixing was continued during the whole investigation period. Every 24 hours (except for Saturdays and Sundays) one bottle was sacrificed for analysis. The analysed parameters included: suspended solids (SS), volatile suspended solids (VSS), VFAs (using capillary gas chromatography), chemical oxygen demand COD in filtered and unfiltered samples, alkalinity, pH and redox potential. The results obtained were used for calibration of prefermentation model – estimation of hydrolysis coefficients for the primary sludge from each WWTP. Hydrolysis of protein nitrogen was neglected due to lack of reliable data from full-scale installation.

The estimated factors were used to simulate the performance of prefermenters from the considered WWTPs in their real configuration. Results of simulation were compared to operational data: for the Jaworzno WWTP from 2 months (February-March 1997) and for the Jaslo WWTP from 4 months (March –June 1997).

### **Prefermenter Design in the Jaworzno WWTP**

A pre-fermentation process in this plant takes place in the completely mixed reactor. According to the project the sludge from the primary clarifier in the amount of 145 m<sup>3</sup>/day would have been pumped continuously to the prefermenter of 290 m<sup>3</sup> volume, which would provide HRT (and SRT) of 2 days. Sludge from the prefermenter is returned to the inlet of primary clarifier: the sludge storage volume of the primary clarifier was 47 m<sup>3</sup>. Prefermenter would have been equipped with a mechanic mixer. However, during the plant completion the mixer was not installed for financial reasons, which worsened the reactor hydraulic conditions. In addition, the capacity of the plant did not reach the design value and at the time of investigation it was only 30% of this. Consequently, the technological conditions and parameters of pre-fermentation process were - during the research period - significantly different from those assumed in the project and generally recommended in the literature. The actual SRT was as long as 9 days.

### **Prefermenter Design in the Jasło WWTP**

The pre-fermentation process in the Jasło WWTP takes place in two primary sludge gravity thickeners (static prefermenters), each of 191 m<sup>3</sup> volume. The thickeners are equipped with slow mechanic mixers. The project assumed that the amount of incoming sludge would be 108 m<sup>3</sup>/d to each of the thickeners, which results in HRT of 1,8 days. During this study, the capacity of the plant was close to the design. However, also in this case the prefermenters operational parameters significantly differed from the values assumed in the project. During our investigations the average SRT in the static prefermenters, calculated on the basis of available operation data, was up to 5,4 days. It was caused by low effectiveness of SS removal in the primary clarifiers.

## **DISCUSSION OF RESULTS.**

### **Batch Tests**

A hydrolysis rate constant for soluble substrate ( $k_{h,s}$ ) and a hydrolysis rate constant for insoluble substrate ( $k_{h,is}$ ) have been determined for the primary sludge from Jaworzno and Jasło WWTPs. The constants were determined using the DSP simulation for a batch fermenter. The results of the simulation are shown in figures 1 and 2, which also show the values obtained in the analytical experiments. The simulation also included changes of pH in the batch tests. The estimated hydrolysis rate constants with their goodness of fitness (GoF) are shown in Table 1

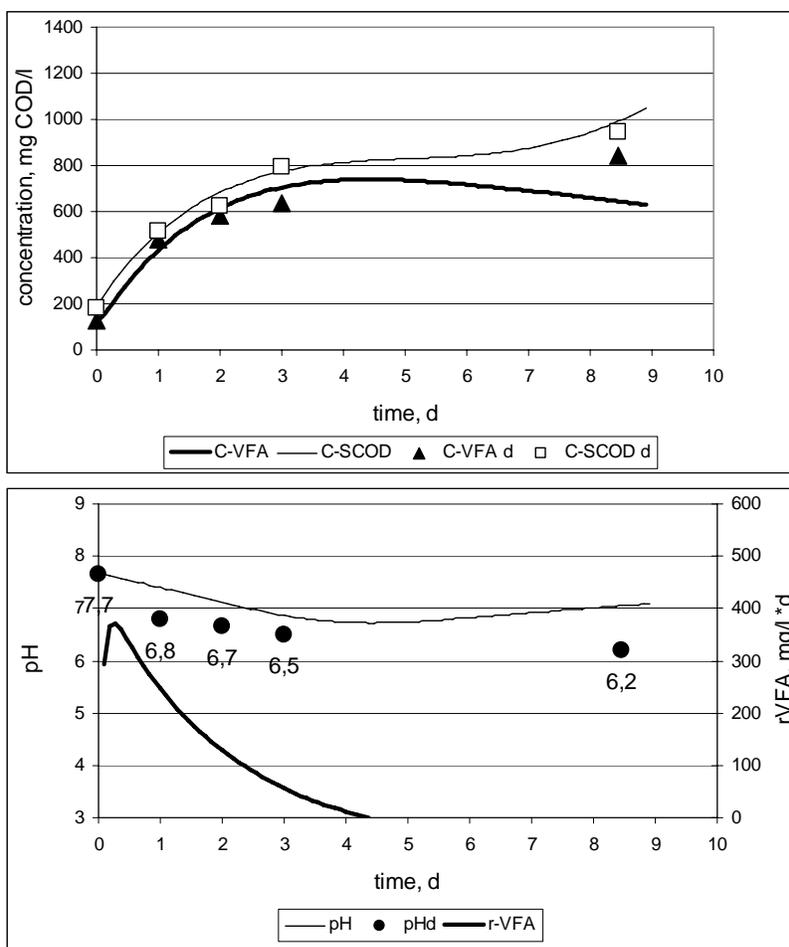
**Table 1.** Values of the fitting parameters – hydrolysis rate constants for batch test.

Parameter	Sludge from plant	
	Jaworzno	Jasło
$k_{h,s}$ (1/mg d)	2.45	0.03
GoF $_{k_{h,s}}$ (%)	81.2	72.6
$k_{h,is}$ (1/d)	1.56	0.1
GoF $_{k_{h,is}}$ (%)	94.1	76.63
$\Sigma$ GoF (%)	87.7	74.2

A comparison of the rate constants shows that higher values obtained for the sludge from Jaworzno indicate faster VFAs generation from the soluble substrates as well as higher SCOD production from the insoluble substrates. The maximum rate of VFA production, defined in this model, was 370 mg VFA/l \*d for the sludge from Jaworzno and 150 mg VFA/l \*d for the sludge from Jasło (see figures 1 and 2).

The better goodness of fitting (GoF) for the constants was found for Jaworzno WWTP. Literature data (Münch et al., 1999b) shows that in other WWTPs cases, the constants were determined with the lower GoF values - between 24 and 79% - which means that the fitting of model to the research data for both WWTPs can be regarded satisfactory.

According to Münch (1998) the average values of fitted kinetic parameters are  $k_{h,s}=0.75$  l/mg d and  $k_{h,is}=0.25$  l/d. These values are lower than the one obtained during the simulation for the Jaworzno WWTP but higher than those obtained for the Jasło WWTP. However, the data set obtained for the WWTPs in Australia and Canada by Münch (1998) shows that the values cover quite a wide range:  $k_{h,s}$  from 0.012 to 3.01 l/mg d;  $k_{h,is}$  from 0.092 to 0.5 l/d. Therefore, it may be concluded that the fitted parameters show a value for hydrolysis rate constant for insoluble substrate for Jaworzno outside respective range. However, due to the high goodness of fitting (94.1%) the result was assumed correct.

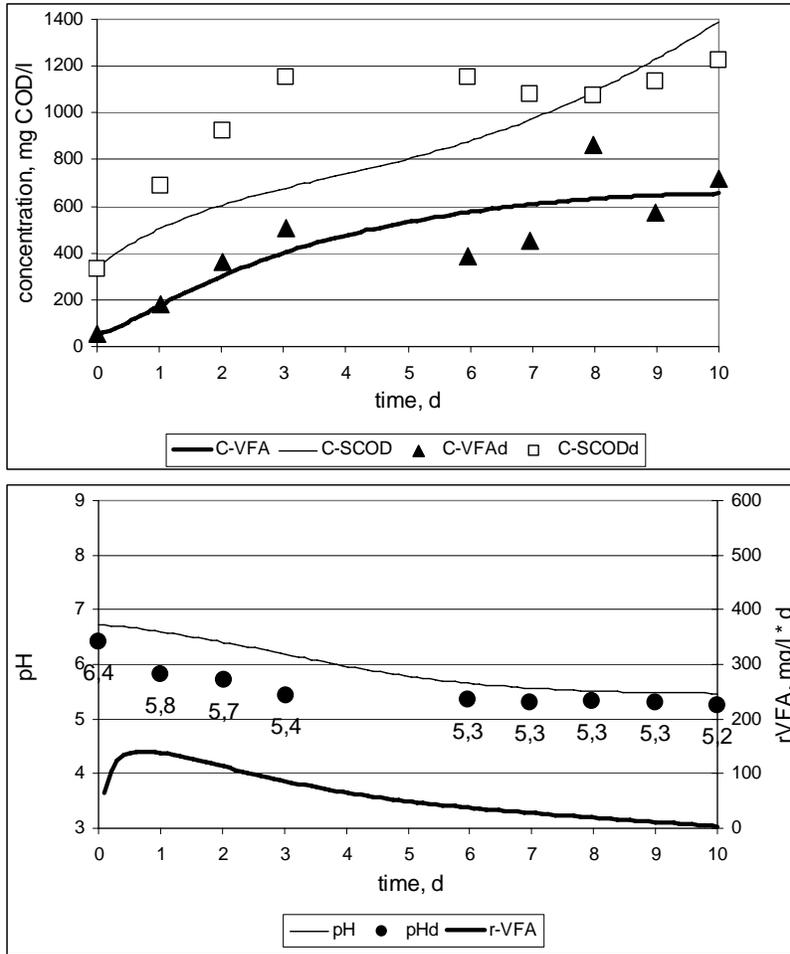


**Figure 1.** Simulated VFAs and SCOD concentration, pH and rate of VFAs production for batch test with sludge from Jaworzno WWTP

A measurement of an actual pH values were also compared to the values obtained in the simulation. The results are also presented in figure 1 and 2; they show that pH values from modelling are rather overestimated comparing to the experimental data.

### Operational Data Simulation

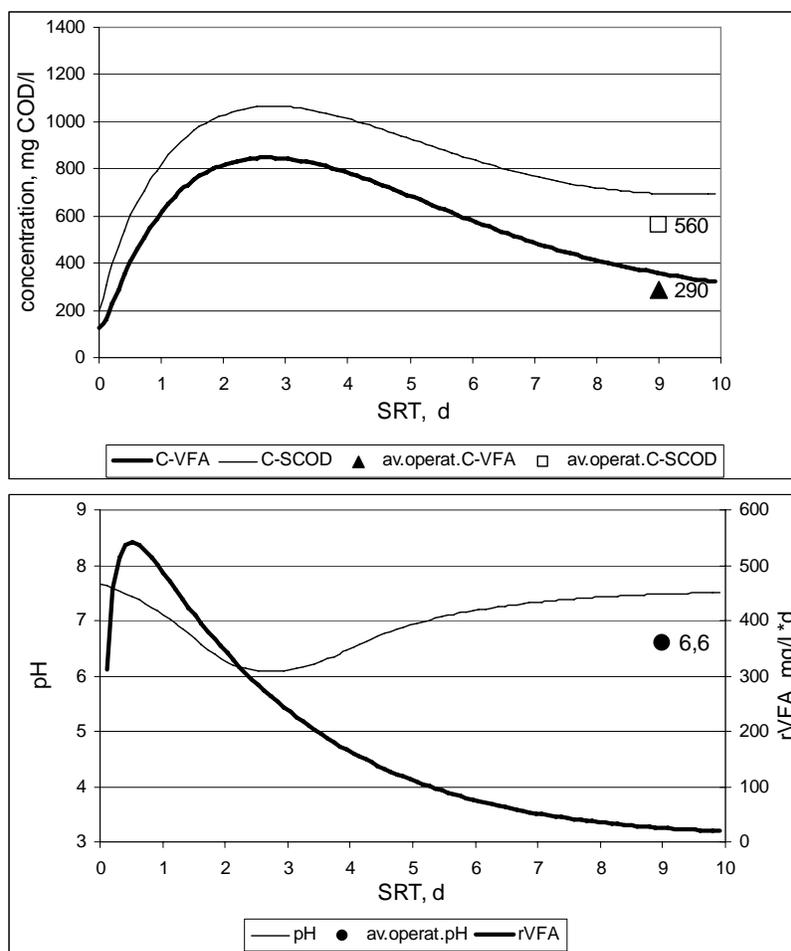
Operational data simulation has been conducted using the kinetic constants estimated empirically (as described in the previous chapter). A steady state simulation has been assumed because of the insufficient quality of data available from WWTP. The data allowed for calculation of the average values for longer time periods, but not for monitoring their changes with correlation to particular parameters. Some of the results from the WWTPs seems questionable; therefore the obtained results should be treated only as approximation.



**Figure 2.** Simulated VFAs and SCOD concentration, pH and rate of VFAs production for batch test with sludge from Jaslo WWTP

The results of the simulation, which show the predicted performance of the prefermenters in relation to SRT are shown in figures 3 and 4. Also the real average values, calculated from operational data, are marked in these figures. To highlight better the operational results concerning VFA generation in the analysed WWTPs, cummulation curves of daily VFA concentration variability for longer periods of time were shown in figures 5 and 6. These period covered investigation period which averages are shown in figures with computer simulation.

The simulation results for a completely mixed prefermenter in Jaworzno (shown in fig. 3). indicate that its SRT optimal range is 2 - 4 days and that in such case, the maximally obtainable VFAs concentration would be about 800 mg VFA(COD)/l. The agreement of the average operational results and the modelled process performance seems satisfactory. In the case of a prefermenter operated at longer SRT, its potential possibilities are not fully utilized. As the data in fig. 5 shows, such high values were not achieved in practice of prefermenter operation in Jaworzno. The VFA concentrations for  $p = 50-90\%$  ranged only 300-400 mg VFA (COD)/l.



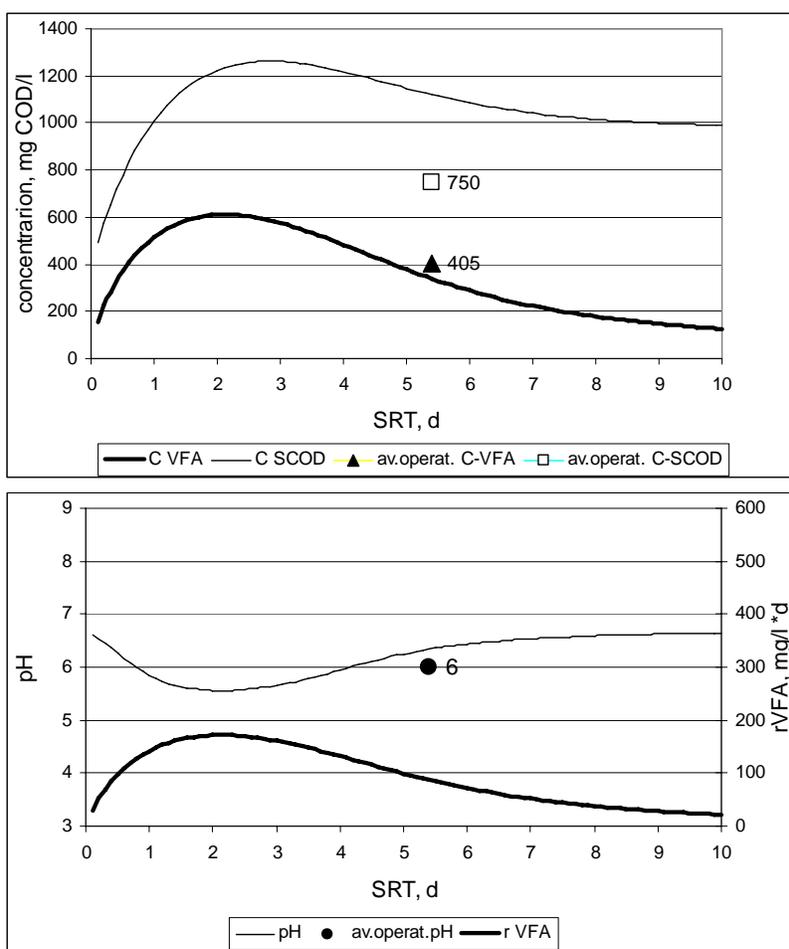
**Figure 3.** Simulated VFA and COD concentration, pH and rate of VFA production for Jaworzno prefermenter in relation to SRT. The points indicates average operational data.

The simulation results for a static prefermenter in Jaslo, shown in Fig.4, indicate that the optimal for its operation is the SRT of 1.5 – 3 days; the VFA concentration would then reach about 600 mg VFA(COD)/l. The conformity of average operational results with a model is also satisfactory. In case of a prefermenter in Jaslo, which is operated at longer SRT, its potential is not used as well. The VFA concentration range, obtained during an every-day operation, for  $p = 50-90\%$  is 280-500 VFA (COD)/l.

The comparison of simulated pH values with the actual ones (see Fig. 3 and 4) shows that lower pH values were observed in prefermenter; it means that the simulating program has a tendency to overestimate this parameter.

The simulation also indicates that actually operated prefermenters produce VFAs at rather slow rate; for Jaworzno about 30 mgVFA/l\*d (with definitively too long SRT) and for Jaslo about 90 mgVFA/l\*d. The probable cause is too long SRT which favors methanogenesis consuming generated VFAs. However, it should be noticed that regardless of not-optimized SRT also other factors could contribute to the fact that an actual efficiency is lower than the one predicted in the simulation. Münch (1998) points out that the results of the batch tests are usually higher if

compared with the operational data from fermenters. Better mixing or higher biomass activity during the experimental conditions may be the cause of such phenomena.



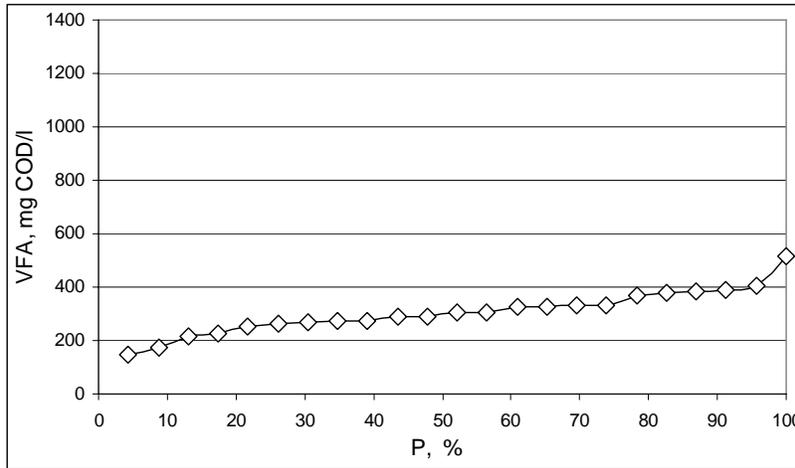
**Figure 4.** Simulated VFA and COD concentration, pH and rate of VFA production for Jaslo prefermenter in relation to SRT. The points indicates average operational data.

To compare the efficiency of discussed Polish prefermenters with other units the operational results of other fermenters of similar configurations were presented in table 2.

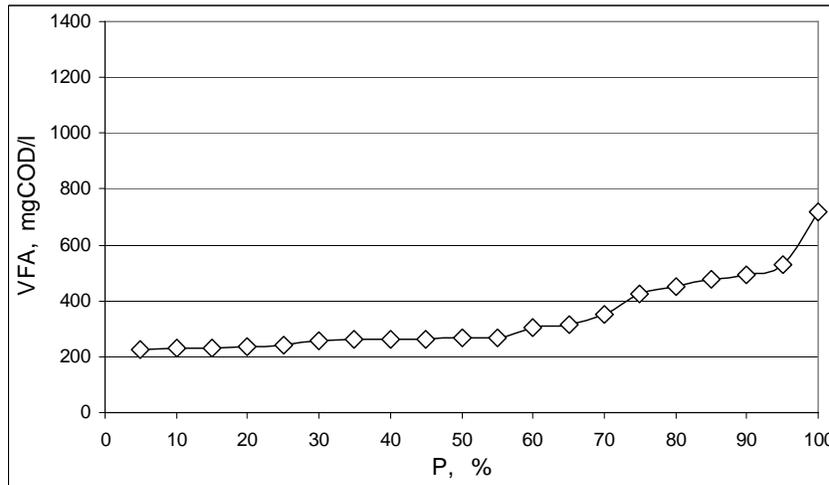
**Table.2.** Prefermenter operational data and calculated rates of VFA production. (Münch E., Koch F.A., 1999)

Plant	Prefermenter type	SRT d	C-VFA <sub>eff</sub> mg COD/l	r VFA mg/l d
Pentrieth	Complete-mix	1.8	758	348
Rouse Hill	Complete-mix	6.9	891	96
Kelowna	Static fermenter	4-8	267	672
Westbank	Static fermenter	4-8	206	348

From the data shown in table 2, it may be concluded that the efficiency of prefermenters in Jasło and Jaworzno is not very high, especially in case of the VFAs production rate. In practice higher VFAs concentration are usually obtained for complete mix prefermenter, which means that the process efficiency in case of the Jaworzno WWTP is very unsatisfactory. However, two examples of the static fermenters presented by Münch E., Koch F.A. (1999) showed that their operation at the longer SRT gives a VFA generation efficiency similar to the one obtained in the simulation for Jasło WWTP (in spite of much higher VFA production rates in these WWTPs). That is probably connected with the difference between the SRT and a hydraulic retention time – HRT; HRTs for static prefermenters in Kelowna and Westbank WWTPs were 3 to 4 times shorter than that for Jasło.



**Figure 5.** Probability diagram of VFA concentration for Jaworzno prefermenter during the period of investigation.



**Figure 6.** Probability diagram of VFA concentration for Jasło prefermenter during the period of investigation.

## **CONCLUSIONS**

Application of the DSP program to simulate the pre-fermentation process is a solution for optimisation of process operational conditions. Employment of the program at the WWTP has to go together with a prefermenter monitoring system, since the prefermenters working currently in Poland usually do not have any instruments allowing for a reasonable process control and monitoring. The advantages of computer simulations, in evaluation of potential of higher VFA generation for the biological nutrients removal process, were shown in this paper. Additionally, pre-design research work and DSP simulation could help designers to assess the need of the pre-fermentation process and also choose the optimal pre-fermentation technology.

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