Reaction rate coefficient k_{20} and temperature coefficient Θ in organic waste thermal disintegration

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Abstract. It was described the test of sewage sludge and organic fraction of municipal mixed solid waste thermal disintegration process. The waste activated sludge used during the tests was collected from the secondary settlement tank in a mechanical-biological wastewater treatment plant. The biowaste used in the studies was collected from an area of new buildings. It was noticed from means values of Soluble Chemical Oxygen Demand (SCOD) plot that both heating temperature and time, influence the amount of dissolved COD. The observations indicate that changes of SCOD can be described by an increasing, differentiable function of time and the rate of change of the soluble COD in the hydrolysates, in time is proportional to the difference of the maximum values of SCOD and its value in time, which leads to the relationship of the first-order ordinary differential equation. The process effectiveness depending on the temperature was described with the mathematical model including Van't Hoff-Arrhenius equation. Inspection of the data and some preliminary fits indicates, that for the description of changes in SCOD terms of time and temperature were adopted the form of nonlinear mixed model. Values of k_{20} indicator and Θ parameter depend on the substrate type. For waste activated sludge thermal disintegration, value of reaction speed indicator k_{20} was 0.028 h^{-1} (0,67 d^{-1}), and value of temperature indicator equalled Θ = 1.024. For thermal disintegration of biological waste, value of reaction speed indicator k_{20} was 0.016 h^{-1} (0,38 d^{-1}), and value of temperature indicator equalled Θ = 1.016.

1 Introduction

Chemical Oxygen Demand (COD) is the fundamental parameter used in modelling (e.g. ASM3, ADM1) and optimization of biochemical processes which specifies organic substrates. Due to its fractioning properties, COD provides information about the content of soluble, particle, biodegradable and hard degradable substances [1]. The effect of activated sewage sludge thermal disintegration on the content change in obtained hydrolysates most recently is tested in order to check the possibilities of accelerating hydrolysis process which limits biodegradation both under aerobic and anaerobic conditions.

The Van't Hoff-Arrhenius equation describes the relationship between the reaction rate constant k and temperature T *(A* is the pre-exponential factor, a constant for each chemical reaction*; R* is the universal gas constant)*:

$$k = A \cdot e^{-E/R \cdot T'}. \tag{1}$$

The Arrhenius equation is true for the majority of simple chemical reactions and the E coefficient has a clearly specified physical sense only for them. For complex reactions, the Arrhenius equation may be fulfilled when the total reaction rate is equal to rate of its slowest step. In case of treatment of the wastewater with the use of activated sludge, equation (1) may be expressed in the following form:

$$k_T = k_{20} \cdot \Theta^{(T-20)}, \tag{2}$$

where:
T - temperature, ^{o}C;
k_{20} - coefficient of reaction rate, h^{-1} at ambient temperature (20°C);
Θ - temperature coefficient.

The higher the value of temperature coefficient Θ, the greater is the impact of temperature on the rate of substrates degradation. The value of temperature coefficient set for the processes run in different technological conditions was specified in Table 1.

Table 1. Temperature coefficient Θ for different biochemical processes [2].

Process	Coefficient Θ
activated sludge load a) > 0.5 kg BOD_5 (kg d.o.m.·day)$^{-1}$ b) < 0.5 kg BOD_5 (kg d.o.m.·day)$^{-1}$	1.0 1.0-1.04
aerobic ponds	1.035
anaerobic ponds	1.070-1.080
nitrification process	1.120
denitrification process	1.060-1.130
anaerobic digestion of sewage sludge	1.07 -1.066

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In spite of elaborating upon other relationships in the subsequent years, at present, equation (2) is used most frequently in determining the impact of temperature on the processes of biological treatment of wastewater with the use of activated sludge.

Temperature also has a decisive influence on the growth and development of all organisms. The temperature depends on the speed of chemical reactions and the physico − chemical state of protein and nucleic macromolecules. Increasing the temperature accelerates the biochemical reactions taking place in the cell which has a positive effect on the growth rate. On the other hand, high temperature can lead to irreversible deactivation and degradation of cell components that are sensitive to high temperature (nucleic acids, proteins and others) which can result in growth inhibition or cell death. Most enzymes are quickly inactivated above 70°C but there are enzymes such as, for example, ribonuclease that are able to survive in an active state for some time at about 100°C [3].

High temperature heat-induced denaturation of proteins is the greatest threat to the speed of enzymatic processes. The sensitivity to the temperature of various proteins in the cell, however, varies. Often, after elevating the temperature, only some proteins are damaged which slows down processes or limits their growth. After reaching the limit temperature, the cell processes become deregulated and cell death occurs. However, this does not necessarily mean that all cellular proteins have denatured. It is enough to denature one of the most important enzyme proteins that catalyzes the necessary biochemical reaction [4].

The speed of the process consisting of a sequence of related reactions is determined by the slowest reaction. From the point of view of the kinetics of the process, hydrolysis is the rate limiting phase, e.g. methane fermentation of substrates with a high content of constant fractions [5]. For some of the organic compounds, hydrolysis is the final stage of degradation, as only part of the substance is further degraded to gas products. The remaining amount of complex organic substances is not biodegradable due to the unavailability of appropriate depolymerising enzymes and the size of hydrolyzed particles [6].

According to the *Adsorption based kinetic model* (ABK model) [7], the hydrolysis rate of insoluble substrates increases with increasing enzyme concentrations, the amount of adsorbed easily biodegradable substrate and the degree of particle disintegration. Tong [8] also observed a correlation between the rate of hydrolysis and the degree of biodegradation of organic matter.

The constant hydrolyses for the first order (k_h) reactions of the basic groups of organic compounds is summarized in Table 2. The constant values of enzymatic hydrolysis of sewage sludge and selected wastes are summarized in Table 3.

The constant values of hydrolysis reported in the literature for the same compounds or wastes vary within very wide limits. The reason for this variation is the significant influence of the chemical composition and the size of solid waste particles on the course of the methane fermentation process. Determination of kinetic constants for bio-waste requires consideration of process conditions such as temperature or pH which causes additional difficulties [9].

Table 2. The constant hydrolyses for the first order (k_h) reactions of the basic groups of organic compounds.

Substrate	k_h, d^{-1}	T, °C	References
Fats	0.76	-	Shimizu [10]
	0.63	25	Masse [11]
	0.1-0.7	-	Garcia-Heras [12]
Carbohydrates	0.025-0.200	55	Christ [13]
	0.5-2.0	-	Garcia-Heras [12]
	0.240	-	Borges [14]
Protein	0.015-0.075	55	Christ [13]
	0.25-0.8	-	Garcia-Heras [12]
	0.099	-	Borges [14]
Cellulose	0.04-0.13	-	Gujer [15]
	0.1	35	Noike [16]
	0.066	35	Liebetrau [17]

Table 3. The constant values of enzymatic hydrolysis of sewage sludge and selected wastes.

Substrate	k_h, d^{-1}	T, °C	References
Waste			
Kitchen waste	0.03–0.15	20	Veeken [18]
	0.24–0.47	40	Veeken [18]
	0.34	35	Liebetrau [17]
	0.55	37	Vavilin [19]
Biowaste	0.12	35	Liebetrau [17]
Municipal solid waste	0.03–0.15	20	Veeken [18]
	0.10	15	Bolzonella [20]
Manure	0.13	55	Vavilin [21]
Paper	0.036	35	Vavilin [19]
Cardboard	0.046	35	Vavilin [19]
Sewage sludge			
Primary sludge	0.99	35	Ristow [22]
Waste activated sludge	0.17–0.6	35	Ghosh [23]
Mixed sludge	0.12	35	Borges [14]

2 Methodology

The aim of the research was to determine the value of reaction rate coefficient k_{20} and temperature coefficient Θ for biowaste and waste activated sewage sludge thermally disintegrated.

2.1. Experimental procedures

It was accompanied the substrates thermal disintegration process with a number of tests. The waste activated sludge (WAS) used during the tests was collected from the secondary settlement tank in a mechanical-biological wastewater treatment plant with the capacity Q = 6,450 $m^3 d^{-1}$. This plant is working under the low-loaded active sludge technology. This technological system does not include a primary settlement tank and the process of biological treatment is conducted in nitrification, denitrification and dephosphatation processes. Additionally, phosphor removal is supported by the precipitation reaction. Municipal solid waste were collected from the area of new buildings. The experimental material consisted of segregated waste fraction from 0 to 80 mm (Table 4).

Table 4. The composition of municipal solid waste from the area of new buildings (w/w, average value) (own study).

Category	Participation, %
Fraction <10 mm	6.7
Fraction 10-20 mm	4.4
Kitchen and garden waste	26.3
Glass	16.8
Plastics	15.1
Paper and cardboard	11.4
Multi-material waste	5.1
Metal	2.0
Mineral waste	1.1
Fabrics	1.6
Wood	0.3
Hazardous waste	0.1
Others	9.1

For this purpose, glass, paper, plastics, metals, textiles, mineral waste and others have been sorted out from waste. The remaining part of the waste was divided into characteristic components and their share in the total mass of the sample was determined. On this basis, samples for testing were prepared each time.

Substrates was treated at the following temperatures: 55, 75, 95, 115, 135, 155 and 175°C for 0.5, 1 and 2 hours. Samples were treated at the given temperature in an autoclave Zipperclave 1.0., Autoclave Engineers. The autoclave warm-up time lasted 10 – 20 min depending on the required temperature, and the maximum cooling time was 15 min. In each time and temperature three repetitions were made. Each measurement was made separately for a certain heating time at the changing temperature.

The evaluation of substrates thermal disintegration effect on the change of the hydrolysates profile was performed on the basis of physical and chemical analyses of raw and post-treatment samples. In this case COD with its fractions were performed according to the current methodology before and after the disintegration process. For this paper, COD measured on hydrolysates will be called "soluble COD" (SCOD).

2.2 Characteristic of substrates

Value of the total COD in raw WAS added to thermal disintegration was changed in the range of from 6,625 to 6,940 gm^{-3}, with an average value at $6,843 \pm 107$ gm^{-3}. The content of COD soluble fraction was 4.6% (average value 272 gm^{-3}).

Value of the total COD in raw biowaste added to thermal disintegration was changed in the range of from 72,800 to 76,900 gm^{-3}, with an average value at $7,510 \pm 1,700$ gm^{-3}. The content of COD soluble fraction was 0.5% (average value 404 ± 26 gm^{-3}).

2.3 Mathematical modelling

The observations indicate that changes of SCOD can be described by an increasing, differentiable function $S(t)$ of time. The rate of change of the soluble COD in the hydrolysates, at time t is proportional to the difference of the maximum values of SCOD and its value in time t, which leads to the relationship:

$$\frac{dS(t)}{dt} = -k \cdot (S(t) - S_{max}), \quad k>0, \qquad (3)$$

where:
S_{max} - asymptotic maximum value.
This is the first - order ordinary differential equation. Taking into account the initial condition as S_0 at time $t_0 = 0$ recorded as $S(t_0) = S_0$, we obtain the solution:

$$S(t) = S_{max} - (S_{max} - S_0) \cdot e^{-kt}. \qquad (4)$$

The process effectiveness depending on the temperature was described with the mathematical model including Van't Hoff-Arrhenius equation (2). This is demonstrated in the following equation:

$$S_T(t) = S_{max} - (S_{max} - S_0) \cdot e^{-k_{20} \cdot \Theta^{(T-20)} \cdot t}, \quad (5)$$

where:
t — disintegration time, h;
T — determined disintegration temperature, °C;
k_{20} — coefficient of reaction rate, h^{-1}, $k_{20}>0$;
Θ — temperature coefficient, $\Theta>0$.

Using equation (5) and the SCOD values obtained in hydrolysates the coefficient of reaction rate k_{20} and the temperature coefficient Θ were determined.

3 Results and discussion

It was noticed from means values of SCOD plot that both heating temperature and time, influence the amount of soluble COD (Fig. 1 and 2).
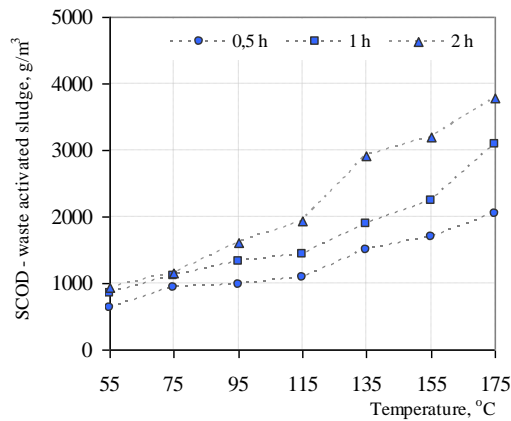
Fig.1. Changes of soluble COD (SCOD) depending on temperature and disintegration time – waste activated sludge.
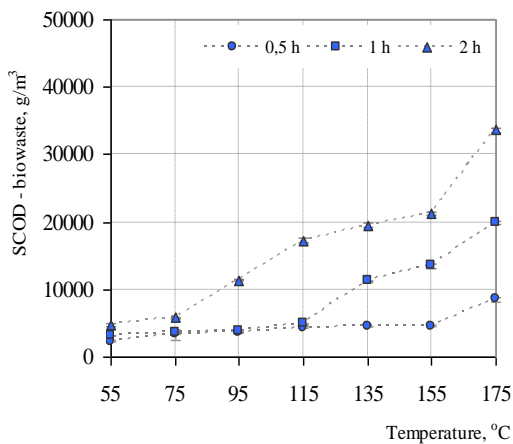
Fig.2. Changes of soluble COD (SCOD) depending on temperature and disintegration time – biowaste.

Thermal treatment of WAS through the period of 0.5 hour resulted in the increase in SCOD content from 5% (55°C) up to 27% (175°C). Achieving the comparable effects at lower temperatures is the consequence of prolonging disintegration time to 1 and 2 hours. For example, the SCOD content increased by 25% during one-hour treatment at 155°C and the comparable effect (23%) was observed at 115°C after 2 hours. The best effect was obtained for excessive sludge disintegrated at 175°C for 2 hours. In this sample, SCOD content amounted to 54%.

Thermal treatment of biowaste through the period of 0.5 hour resulted in the increase in SCOD content from 3% (55°C) up to 11% (175°C). Achieving the effects greater then 10% required a temperature of 135°C (15%) for 1 hour, and in the process of low temperature disintegration it required extending the treatment time to 2 hours. The best effect was obtained for excessive

sludge disintegrated at 175°C for 2 hours. In this sample, SCOD content amounted to 44%.

The tests confirmed the literature data [24] on high effectiveness of organic waste hydrolysis and the possibility of solid fraction liquidation process above 40%.

Inspection of the data and some preliminary fits indicates, that for the description of changes in SCOD terms of time and temperature were adopted the form of nonlinear mixed model:

$$y_{ij} = \beta_1 - (\beta_1 - (\beta_2 + b_i)\exp(-k_{20}\Theta^{(T_{ij}-20)}t_{ij})) + \varepsilon_{ij}, (6)$$

where:
y_{ij} - the value of SCOD for the jth of 7 observations in the ith of 9 clusters (the waste activated sludge and biowaste samples);
t - the disintegration time;
T - temperature;
k_{20} - the fixed coefficient of reaction rate;
Θ - the temperature coefficient;
β_1 and β_2 - the fixed population coefficients, which are identical for all clusters;
b_i - the individual random effect for group i, that varies appreciably from sample to sample, assumed to have a normal distribution with mean zero and variance σ^2_{sludge}.

It is assumed that observations made on different clusters are independent and ε_{ij} are independent and normal with mean zero and variance σ_e^2 and are independent of the b_i. The estimates of fixed coefficient obtained from this nonlinear mixed model (6) are presented in Table 5 and 6. Thus, parameter β_1 represents the maximum SCOD value and β_2 determines the expected initial value. The mixed parameters of $\beta_2 + b_i$ determine the initial value of SCOD, which may vary depending on the sample. The adopted model demonstrated statistical significance of its effect (p-value=0.0198 and $\hat{\sigma}^2_{sludge}$=93.4112, $\hat{\sigma}_e^2$=125.8091).

**Table 5.** Fixed effects from the mixed nonlinear model with SCOD as the response – waste activated sludge.

Parameter	Estimate	Std. Error	Wald test	p-value
β_1	4259.878	162.9601	26.1406	<0.0001
β_2	641.842	64.0006	10.0287	<0.0001
k_{20}	0.028	0.0048	5.7956	<0.0001
Θ	1.024	0.0013	799.4359	<0.0001

**Table 6.** Fixed effects from the mixed nonlinear model with SCOD as the response – biowaste.

Parameter	Estimate	Std. Error	Wald test	p-value
β_1	101501.5	45464.77	2.233	0.0294
β_2	101505.1	45209.59	2.245	0.0285
k_{20}	0.016	0.007712	2.051	0.0447
Θ	1.016	0.000982	1034.794	<0.0001

On the graph showing (Fig. 3 and 4) a graphical diagnostic assessment of the quality of the fit of the nonlinear mixed model for the SCOD values obtained.
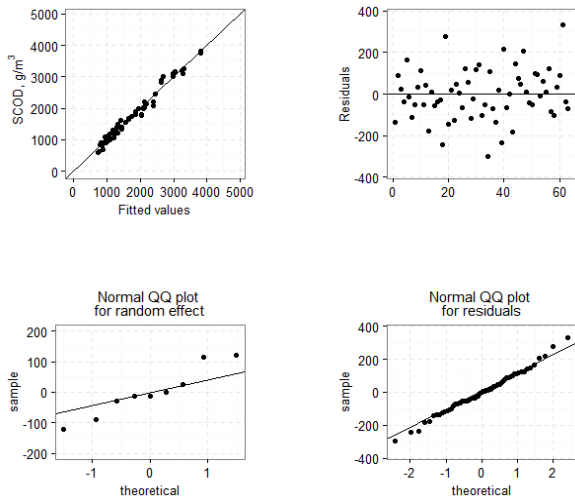
Fig. 3. Residuals, fitted values and Normal quantile-quantile plots for assessing the fit of nonlinear mixed model for SCOD – waste activated sludge.
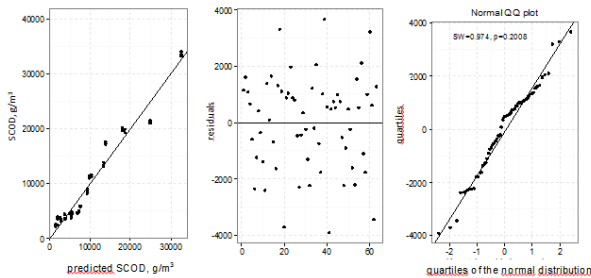
Fig. 4. Graphic assessment of the fit of a mixed logistics model - biowaste.

For waste activated sludge thermal disintegration, value of reaction speed indicator k_{20} was 0.028 h^{-1} (0,67 d^{-1}), and value of temperature indicator equalled Θ = 1.024. For thermal disintegration of biological waste, value of reaction speed indicator k_{20} was 0.016 h^{-1} (0,38 d^{-1}), and value of temperature indicator equalled Θ = 1.016.

The value of reaction rate coefficient k_{20} depends on the type of substrate, and in literature data amounts to, e.g. k_{20}=0.997 h^{-1} for proteins, k_{20}=0.2404 h^{-1} for hydrocarbons, k_{20}=0.0272 h^{-1} for lipids and k_{20}=0.1216 h^{-1} for sewage sludge [18, 19, 23]. The value of this coefficient increases proportionally to substrate hydrolysis rate and its assimilation.

The value of Θ coefficient which describes the temperature effect on reaction rate is presented in the literature in the range from 1.013 (sewage sludge) to 1.066 (hydrocarbons) [14]. The value of this coefficient increases along with the increase in temperature effect on the decomposition rate, and thus substrates biodegradability.

Not only solid fraction liquidation level of sludge, but also the form of organic compounds arising from the

disintegration process decides about the biodegradation possibility. As many authors demonstrated in their tests, the determined optimal conditions for performing the process are not identical for all substrates. Barlindhaug and Odegaard [25] advanced a hypothesis that hydrocarbons are more susceptible to mineralisation than proteins during the thermal treatment process. However, proteins can undergo liquidation more easily. Therefore, the precise evaluation of substrate quality before initiating the disintegration process is purposeful.

4 Conclusions

The analysis of results obtained from performed tests can show that the method of waste activated sewage sludge and biowaste thermal treatment has a positive impact on its characteristics changing its potential susceptibility to biodegradation.

Conducted series of tests demonstrated the content increase of SCOD in total COD in all samples after disintegration.

For waste activated sludge thermal disintegration, value of reaction speed indicator k_{20} was 0.028 h^{-1} (0,67 d^{-1}), and value of temperature indicator equalled Θ = 1.024. For thermal disintegration of biological waste, value of reaction speed indicator k_{20} was 0.016 h^{-1} (0,38 d^{-1}), and value of temperature indicator equalled Θ = 1.016.

References

1. S. Myszograj, Arch. Environ. Prot. **39**, 57 (2013)
2. S. Myszograj, Br. J. Appl. Scie. Technol. **11**, 1 (2015)
3. U. Schmitz, R. Berger, H. Ort, Water Res. **34**, 3682 (2000)
4. I. Syaichurrozi, B.S. Sumardiono, Bioresource Technol. **149**, 390 (2013)
5. P.J. Strong, D.J. Gapes, Waste Manage. **32**, 1669 (2012)
6. S.W. Sötemann, P.Van Rensburg, N.E. Ristow, M.C. Wentzel, R.E. Loewnthal, G.A. Ekama, Water Sci. Tech. **54**, 109 (2006)
7. C.R. South, D.A.L. Hogsett, D.L.R. Lynd, Enzyme Microb. Technol. **17**, 797 (1995)
8. X. Tong, L.H. Smith, P. L. McCarty, Biomass **21**, 239 (1990)
9. V.A. Vavilin, B. Fernandez, J. Palatsi, X. Flotats, Waste Manage. **28**, 939 (2008)
10. T. Shimizu, K. Kenzo, N. Yoshikazu, Biotechnol. Bioeng. **41**, 1082 (1993)
11. L. Masse, D.I. Massé, K.J. Kennedy, Biotechnol. Bioeng. **79**, 43 (2002)
12. J.L. Garcia-Heras, in: J. Mata–Alvarez (ed.), *Biomethanization of the Organic Fraction of Municipal Solid Waste* (IWA Publishing, London, UK), ISBN 9781900222143 (2003)
13. O. Christ, P.A. Wilderer, R. Angerhöfer, M. Faulstich, Water Sci. Tech. **41**, 61 (2000)
14. E.S.M. Borges, C.A.L. Chernicharo, Braz. J. Chem. Eng. **26**, 469 (2009)
15. W. Gujer, A.J.B. Zehnder, Water Sci. Tech. **15**, 127 (1983)

16. T. Noike, G. Endo, J.E. Chang, J.I. Yaguchi, J.I. Matsumoto, Biotechnol. Bioeng. **27**, 1482 (1985)

17. J. Liebetrau, E. Kraft, W. Bidlingmaier, S.G Guiot. (ed.), Proceedings of the Tenth World Congress on Anaerobic (Canadian Association on Water Quality, Montreal, 2004)

18. A. Veeken, B. Hamelers, Bioresource Technol. **69**, 249 (1999)

19. V.A. Vavilin, L.Y. Lokshina, J. Jokela, J. Rintala, Bioresource Technol. **94**, 69 (2004)

20. D. Bolzonella, P. Pavan, F. Fatone, F. Cecchi, Ind. Eng. Chem. Res. **44**, 3412 (2005)

21. V.A. Vavilin, L.Y. Lokshina, X. Flotats, I. Angelidaki, Biotechnol. Bioeng. **97**, 354 (2007)

22. N.E. Ristow, S.W. Sötemann, R.E. Loewenthal, M.C.Wentzel, G.A. Ekama, WRC Report No. 1216/05, Water Research. Commission (2004)

23. S. Ghosh, D.L. Klass, in: D.L. Klass (ed.), *Biomass as a nonfossil fuel source* (American Chemical Society, Washington, 1981)

24. P. Camacho, S. Déléris, V. Geaugey, E. Paul, P. Ginestet, Water Sci. Tech. **46**, 79 (2002)

25. J. Barlindhaug, H. Odegaard, Water Sci. Tech. **34**, 371 (1996)