

Mathematical modelling of waste activated sludge thermal disintegration

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Abstract. Chemical Oxygen Demand (COD) solubilisation was used to evaluate the impact of thermal pretreatment on the transfer of sewage sludge from particulate to soluble phase. It was gathering the experimental data needed for building of empirical mathematical model describing the relation between applied temperature and time and rate of COD solubilisation and degradation. In view of repeated measurements, in order to describe the relationship between changes in the fraction of dissolved COD and the time and temperature, mixed models have been adopted where by fixed factor measurement conditions have been adopted: time and temperature, while the random factor changes the characteristics of waste activated sludge. Linear and logistic nonlinear mixed models were analyzed. The tests demonstrated that all variables are statistically significant in assessing their impact on the efficiency of liquefaction of sludge. On the basis of the estimated model, the temperature rise of 10°C increases degree of disintegration 1.7% above the average treatment time for 0.5h, by 2.6% for 1 hour, and by 3.9% for 2h. COD values decrease between 3 to 23% at temperatures in the range of 55 to 115°C. At higher temperatures COD was reduced in the range of 32 to 44%. Disintegration time did not have the significant impact on the degradation effect.

1 Introduction

The processing and disposal of sewage sludge is one of the most important and complex problems in the operation of municipal wastewater treatment plants. Anaerobic digestion is an attractive technology for the treatment of organic waste, which is a series of biochemical processes by different microorganisms to degrade organic matter under anaerobic conditions. Anaerobic degradation of particulate materials and macromolecules is considered to occur in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In sludge digestion, hydrolysis is the rate-limiting step. If the substrates consist of particulates, bacteria release extracellular enzymes that break down and solubilize organic particulate matter [1].

To improve process efficiency, the most expected approach is to destroy the microbial cells in the sludge. Use of pre-treatment of sewage sludge is aimed at breaking microorganisms' cells and release of intracellular organic matter to the liquid phase. Thermal disintegration of sludge has therefore been introduced to solubilize and convert slowly biodegradable, particulate organic materials to readily biodegradable low-molecular-weight compounds. The hydrolysate liquid is rich in organic compounds, since carbohydrates and fats are transformed into easily decomposable forms, and proteins lose the protective enzymatic structure. Thermal pretreatment is an often used method to improve the properties of sewage sludge, which can not only improve the hydrolysis rate of organic substrates. The positive

impact of the disintegration of sludge is considered in the following aspects, too:

- the higher degree of substrates transformation of volatile fatty acids (VFA),
- the decrease in the final waste mass through greater effectiveness of the dewatering processes and the required volumes of waste treatment and sludge treatment facilities,
- the increase in the biogas production,
- the increase in the degree of mineralisation of the organic matter of sludge,
- the increase in the use of conditioning agents before the dewatering and mechanical thickening processes,
- the recovery of certain desirable components from the sludge, for instance, plant-available nitrogen [2-4].

When thermal disintegration is combined with anaerobic digestion, energy required to perform thermal treatment can be positively balanced by biogas production [5, 6].

Thermal disintegration of activated sewage sludge increases biogas production by 30% up to 225%, methane by 60% and decreases stabilized sludge organic mass by at least 30% [7]. For primary and activated sewage sludge, an increased susceptibility to dewatering was observed [8]. The energy balance demonstrates that, compared to the conventional methane fermentation, the system with thermal disintegration of sewage sludge provides a positive energy balance and allows fermentation chambers of smaller volumes. Li and Noike [9] managed to shorten the required fermentation time by 5 days for excess sludge disintegrated at 170°C for 60

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min. Assuming the reduced dry matter and sludge susceptibility to hydration as the evaluation criterion, the literature data show that the optimal temperature for the process of sewage sludge thermal hydrolysis should be constrained to the range of 160 – 175°C. According to Fisher and Swanwick [10], heating the sewage sludge to the temperature exceeding 180°C before the fermentation process leads to considerable loss of dry matter and the formation of refractory organic compounds (non-degradable COD fractions) in the process liquid. Conducting the process at lower temperatures (60 – 80°C) increases the content of obtained hydrolysate, but requires longer reaction times. Elbing and Dünnebeil [11] demonstrated that the effect of the retention time of sewage sludge in the hydrolyser at the tested temperature on the liquidation result is not as crucial as the treatment temperature.

2 Material and methods

2.1 Experimental procedures

It was accompanied the sewage sludge 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 $Q = 6,450 \text{ m}^3\text{d}^{-1}$. 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.

Activated sewage sludge 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 WAS 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. The degree of disintegration was measured as a fraction of the solubilised organic matter. 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) and the difference between total COD and soluble COD will be called “particulate COD” (PCOD). Mathematical method to describe the results of final effectiveness of pretreatment was used [Eq. 1].

The indicator for the direct assessment of effectiveness, which is most frequently encountered in the literature [12], is the quotient of COD growth for compounds solubilised during the hydrolysis after

disintegration (ΔSCOD) and COD of the particulate fraction in the substrate before disintegration (PCOD) or total COD (TCOD) of the substrate, expressed as follows:

$$\eta_{DI} = \frac{(\text{SCOD}_D - \text{SCOD})}{\text{TCOD} - \text{SCOD}} \cdot 100\% = \frac{\Delta\text{SCOD}}{\text{PCOD}} \cdot 100\% \quad (1)$$

where:

η_{DI} - degree of disintegration, %;

SCOD - COD of the compounds solubilised in the raw substrate, gO_2m^{-3} ;

SCOD_D - COD of the compounds solubilised after disintegration, gO_2m^{-3} ;

ΔSCOD - growth of COD of the compounds solubilised after disintegration, gO_2m^{-3} ;

PCOD - COD of the solid substances in the substrate, before disintegration, gO_2m^{-3} ;

TCOD - total COD of the substrate, gO_2m^{-3} .

2.2 Characteristic of waste activated sludge

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 $6,843 \pm 107 \text{ gm}^{-3}$. The content of COD soluble fraction was 4.6% (average value 272 gm^{-3}). And loss on ignition determined for raw sludge was 70.2% TS and COD/TS average quotient was 1.53.

2.3 Statistical analysis and mathematical modelling

Statistical analysis was performed using the statistical software package R distributed under an open-source license (GPL) R core team [13]. R software was used in order to determine the relation between changes in soluble COD and TCOD decomposition values and both time and disintegration temperature.

These relations were described using two approaches: the mixed linear and mixed nonlinear models. The mixed model approach takes into account the correlated nature of the outcomes. Parameters of mixed models were estimated using the maximum likelihood method. In each model was testing random effects with a likelihood ratio test. To verify the significance of fixed effects the Wald test was used. In the case of all statistical tests, the significance level was defined at 0.05. In each model were required model assumptions verified.

In view of repeated measurements, in order to describe the relationship between changes in the fraction of dissolved COD (SCOD) in hydrolysates and the loss of organic matter (ΔTCOD) and the time and temperature, mixed models have been adopted where by fixed factor measurement conditions have been adopted: time and temperature, while the random factor changes the characteristics of waste activated sludge.

Linear and logistic nonlinear mixed models were analyzed. In the modelling of changes in COD fractions it is accepted that the processing time is a categorical

variable with 3 levels, where the time of 0.5h was established as the reference category.

3 Results

The analysis of results indicates the influence of temperature and disintegration time on SCOD in hydrolysates. An increase of COD solid fraction liquidation (Fig. 1), were observed after increasing temperature of pre-treatment.

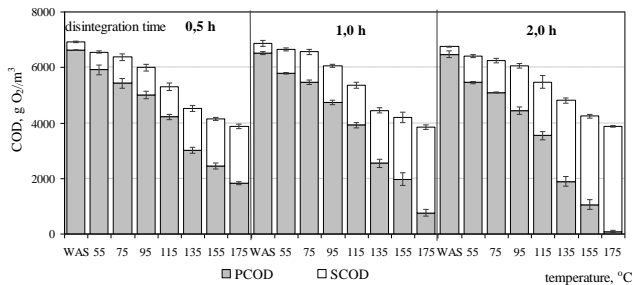


Fig. 1. COD fractions in hydrolysates.

The lowest value for SCOD (281 gm⁻³) was observed in the sample disintegrated at 55°C for 0.5 hour, and the highest value – 3,793 gm⁻³ for the sample treated at 175°C for 2 hours. SCOD content in TCOD in these samples amounted to 4.1 and 97.7% respectively. Regardless of the disintegration time, a significant increase in SCOD values was observed in samples exposed to treatment at minimum 115°C. In disintegration time of 0.5h the highest SCOD value was achieved at 175°C – 2,048 gm⁻³. In the longer disintegration time similar effects were obtained at lower temperatures: 135°C (1h) and 115°C (2h), respectively (and disintegration becomes more complete at high temperatures).

4 Discussion

4.1 Effect of thermal pretreatment on COD solubilization and decomposition

The effectiveness of the disintegration process is evaluated by, inter alia, the increase in soluble COD content in the hydrolysate with relation to the initial value of COD solid fraction according to the Eq. 1 (Fig. 2).

A 26.6% increase in SCOD value was obtained when sludge was pre-treated at 175°C during 0.5 h, a 42.1% was reached at the same temperature when treatment time was 1 h. A 54.2% increase in SCOD was reported at 175°C of the 2 h.

The process of WAS thermal pretreatment in every sample caused the decomposition of organic matter, and consequently resulted in diminishing of total COD value.

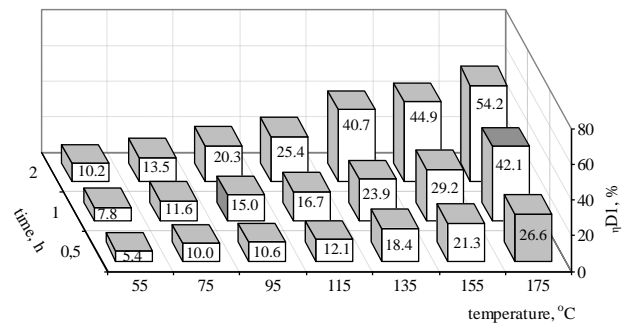


Fig. 2. Changes of η_{D1} value depending on temperature and disintegration time.

Values of SCOD depending on the level of TCOD value decrease in thermal disintegration are illustrated in Figure 3 and 4.

The analysis of results demonstrates that the soluble COD content in hydrolysates at specific treatment temperature increases at a similar relative extent as total COD decreases (Fig. 3).

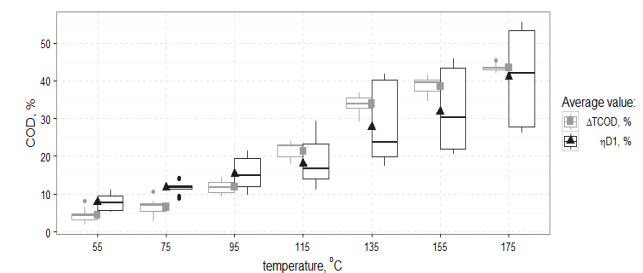


Fig. 3. Box plots and mean value of total COD value by ΔTCOD and η_{D1} versus temperature.

Total COD decrease from 3 to 23% was observed at treatment temperatures in the range of 55 – 115°C. While the disintegration of WAS at higher temperatures affected the reduction of the COD in the range of 32 to 44%. However, the disintegration time did not have the significant impact on the mineralization effect. The decrease of total COD was amounted about 20% in 0.5, 1.0 and 2.0 h pretreatment (Fig. 4).

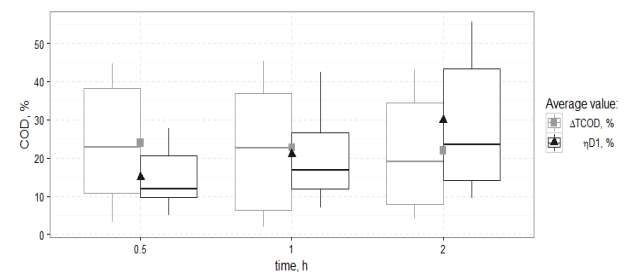


Fig. 4. Box plots and mean value of total COD value by ΔTCOD and η_{D1} versus time.

4.2 The influence of time and temperature on disintegration process efficiency

Values SCOD/TCOD in the pre-treated sludge were clearly higher than that in the raw sludge (Fig.1), thereby indicating that thermal pretreatment had a strong effect

on sludge solubilisation. The degree of effect depending up on the applied temperature and time of treatment. Analysis of mean values and their standard deviations (Fig. 5) demonstrate that changes in the average value of the share of the dissolved fraction of COD (η_{D1}) relative to the process temperatures are linear, but with a different variation in time.

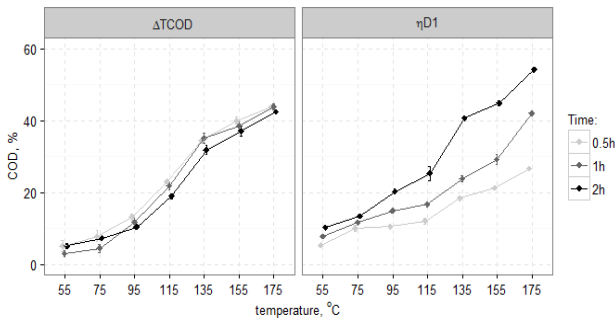


Fig. 5. Mean value and its standard error of total COD value for ΔTCOD and η_{D1} versus temperature by time.

A mixed linear model with regard to the interaction time and temperature has been adopted in modelling the increase in the degree of η_{D1} disintegration. Preliminary analysis demonstrated the absence of a statistically significant random effect in this model ($p\text{-value} = 0.49$), therefore the model has been simplified to the model without considering such an effect:

$$y_i = \beta_0 + \beta_1 x_{temp,i} + \beta_2 x_{time.1h,i} + \beta_3 x_{time.2h,i} + \beta_4 x_{temp,i} x_{time.1h,i} + \beta_5 x_{temp,i} x_{time.2h,i} + \varepsilon_i \quad (2)$$

where y_i corresponds to the i_{th} response η_{D1} , x_{temp} to temperature ($^{\circ}\text{C}$), $x_{time.1h}$ and $x_{time.2h}$ are categorical variables coded with dummy variables 0 or 1, for a heating time 1 and 2h respectively, and ε_i are independent and normal with mean zero and variance σ^2 , $i=1,2,\dots,63$. In this model the heating time 0.5 h was chosen to be the reference category.

In order to verify the relevance of the effect of temperature, time and their interaction on the growth of the degree of η_{D1} disintegration, sequential testing was conducted (Table 1).

Table 1. The sequential tests for the specified effects in the fixed linear model for η_{D1} .

Effect	Sum Sq	Df	F value	p-value
Temperature	7446.9	1	916.471	< 0.0001
Time	2391.6	2	147.164	< 0.0001
Temperature·Time	785.5	2	48.337	< 0.0001

The tests demonstrated that all of these variables are statistically significant in assessing their impact on the efficiency of liquefaction of waste activated sludge. Hence, the impact of temperature on the degree of disintegration is significantly conditioned by the time of treatment ($p\text{-value} < 0.0001$). On the basis of the estimated model (Table 2) the temperature rise of 10°C increases the degree of η_{D1} disintegration approximately

1.7% above the average treatment time for 0.5 h, by 2.6% for 1 hour, and by 3.9% for 2 h.

Table 2. Results of fitting the fixed linear model with η_{D1} as the response.

Parameter	Estimate	Std. Error	Wald test	p-value
Intercept	-4.49881	1.89346	-2.376	0.0209
Temperature	0.16881	0.01555	10.855	<0.0001
Time 1h	-4.75923	2.67776	-1.777	0.0809
Time 2h	-9.80298	2.67776	-3.661	0.0006
Temperature · Time 1h	0.09339	0.02199	4.247	<0.0001
Temperature · Time 2h	0.21560	0.02199	9.803	<0.0001

Regression lines estimated using a linear model (Eq. 2) illustrating the process of η_{D1} change for temperatures of measurements varied by treatment time is presented in Fig. 6.

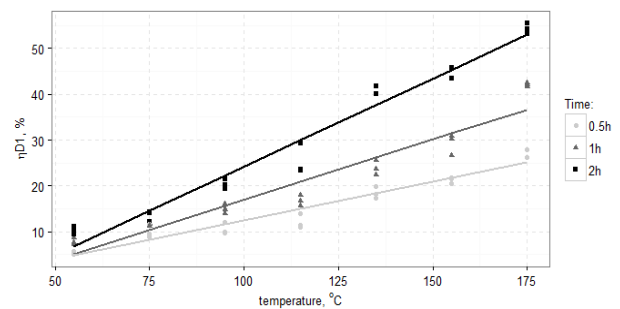


Fig. 6. Scatterplot for η_{D1} versus temperature with linear fit for each group of time.

Analysis of the mean values (Fig. 5) and boxed charts (Fig. 4) demonstrated that the treatment time does not significantly affect the reduction of organic material, measured by COD loss, therefore in this case the dependency of ΔTCOD changes only with respect to temperature was considered. The confidence intervals for the mean ΔTCOD value (Fig. 7) demonstrate that changes in the average COD loss together with increasing temperature of the process are non-linear. The growth rate of TCOD loss is not constant, though varies depending on the temperature. This course suggests that the non-linear logistic model is the adequate model for the description of ΔTCOD changes.

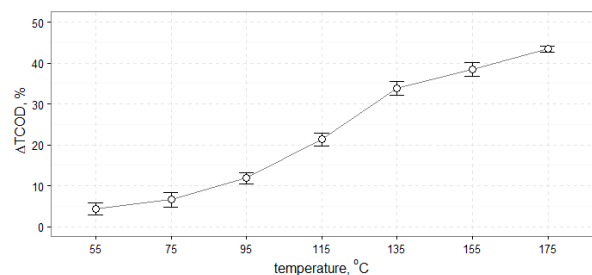


Fig. 7. Mean value of ΔTCOD with 95% confidence intervals versus temperature.

A mixed logistic model was used to analyze the observed behaviour. All parameters were assumed to be fixed and random [15]. The mixed effects logistic model can be expressed as:

$$y_{ij} = \frac{\Phi_{i1}}{1 + \exp(-(x_{ij} - \Phi_{i2}) / \Phi_{i3})} + \varepsilon_{ij} \quad (3)$$

where y_{ij} represents the j_{th} measurement Δ TCOD on the i_{th} sludge sample (cluster), x_{ij} is the corresponding temperature, and ε_{ij} are independent and normal with mean zero and variance σ_e^2 . In this case $i=1, 2, \dots, 9$ and $j=1, 2, \dots, 7$ and all three parameters Φ_{i1} , Φ_{i2} and Φ_{i3} have both a fixed and random component: $\Phi_i = \beta + b_i$, where $\Phi_i = (\Phi_{i1}, \Phi_{i2}, \Phi_{i3})'$, $\beta = (\beta_1, \beta_2, \beta_3)'$ is a vector of fixed population effects, invariant across groups and $b_i = (b_{i1}, b_{i2}, b_{i3})'$ is a vector of individual random effects associated with the i_{th} sludge sample, assumed to have a multivariate normal distribution with mean zero. The variances $\sigma_{sludge,k}^2$ ($k=1,2,3$) and covariances of the random effects are the same in each cluster. It is further assumed that observations made on different clusters are independent and ε_{ij} are independent of the b_i .

The model was analyzed during the construction process and its parameters were determined, assuming a random component. Under normality assumptions, alternative models were evaluated by Akaike information criterion (AIC) (Table 3). A model was selected that only includes the Φ_{i2} parameter (both fixed and mixed components). In addition, it was verified that the random factor is statistically significant in a predetermined fixed effects (p-value=0.001 and $\hat{\sigma}_{sludge,2}^2 = 12.183$, $\hat{\sigma}_e^2 = 3.327$).

Table 3. AIC value for random effect in the mixed logistic model with Δ TCOD as the response.

Random effects	Log-likelihood	AIC
b_1, b_2 and b_3	-131.27	282.54
b_1 and b_2	-133.01	280.01
b_1 and b_3	-133.78	281.55
b_2 and b_3	-132.74	279.49
b_1	-135.32	280.64
b_2	-133.43	276.85
b_3	-138.16	286.32
no random effects	-162.97	333.93

The estimates of fixed logistic parameters obtained with mixed effects models (Eq.3) are presented in Table 4. The predicted logistic curve is shown in Fig. 8, precisely this is the mean curve, i.e., the fitted curve with $b_{i2}=0$ for all i . Model analysis of the logistic model (Table 4) of Δ TCOD changes in relation to temperature differences. At a temperature of 117.7°C (23.53% TCOD loss) the COD loss shows the largest temperature dependence (Fig. 8). More specifically, this temperature is below the rapid depletion of COD during the disintegration process, and above the gradual decrease, the rate of organic matter decreases.

Table 4. Fixed effects from the mixed logistic model with Δ TCOD as the response.

Parameter	Estimate	Std. Error	Wald test	p-value
β_1	47.058	1.076042	43.73237	<0.0001
β_2	117.683	1.989584	59.14946	<0.0001
β_3	22.754	1.076364	21.13963	<0.0001

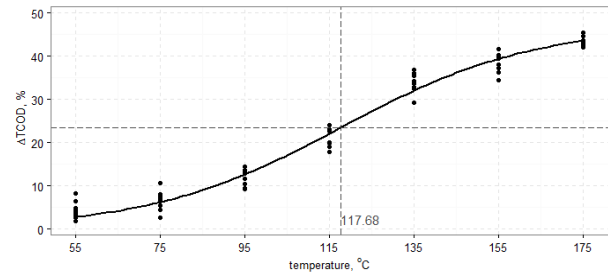


Fig. 8. Scatterplot for Δ TCOD versus temperature and the fitted mean logistic curve.

The graphical evaluation of logistically adjusting the mixed model for Δ TCOD is presented on the diagnostic chart (Fig. 9).

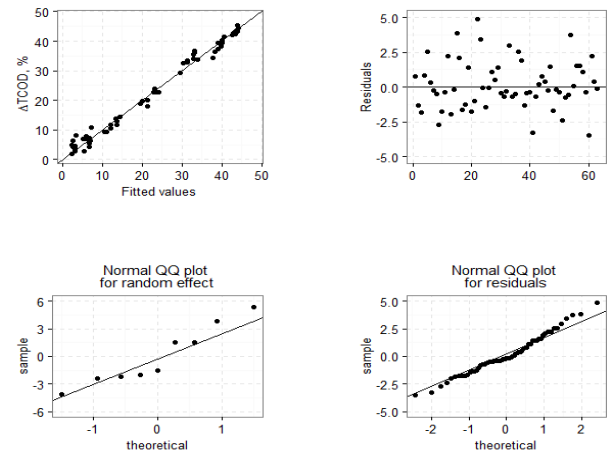


Fig. 9. Residuals, fitted values and Normal quantile-quantile plots for assessing the fit of logistic mixed model for Δ TCOD.

The results are in compatible with that presented in literature. Climent [16] established that the time and temperature have similar influence on the performance of high temperature thermal treatment as well as the combined effect of the two parameters. It should be noted that the degree of solubilisation is in most cases linearly dependent on temperature, especially for high-temperature disintegration. Tanaka [14] were evaluated the effectiveness of thermal treatment by means of SCOD concentration, too. A 25% increase in SCOD value was obtained when sludge was pretreated at 130°C during 30 min, a 30% was reached at the same temperature when treatment time was 60 min. A 60% increase in SCOD was reported at 170°C independently of the time of treatment. Under the same conditions, in Zipperclave reactor, was excessive sludge disintegrated [17, 18] during 15, 30 and 60 min. During the one-hour treatment, the SCOD share increased from 2.7% to 25.3,

43.9 and 59.5% at process temperatures of 130, 150 and 170°C, respectively. Bougrier [19] obtained a solubilisation of the COD fraction in the range of 40 to 45% in 30 and 60 min. However, Aboulfoth [1] at 175°C found an increase in COD solubilisation from 11.2% to 15.1 and 25.1% after increasing the treatment time from 1 to 2 and 3 hours, respectively. Thermal treatment processes are associated with the simultaneous mineralization of organic components, however, it is possible to establish conditions limiting the decomposition [19]. For example Caraballa [20] obtained a reduction of organic mass of sewage sludge below 5%, leading to disintegration at 130°C during 60 min.

5 Conclusions

Thermal (low and high temperature) disintegration is effective in waste activated sludge solubilisation as reflected in the increase of SCOD in hydrolysates.

COD solubilisation was found to increase linearly with treatment temperature. The maximum SCOD value and the majority of the particulate organic matter removals were achieved for the sample treated at 175°C for 2 hours.

It was found, that time and temperature have similar influence on the performance of temperature thermal treatment as well as the combined effect of the two parameters as derived from the coefficients of the mathematical model that results of the experimental data.

References

1. A.M. Aboulfoth, E.H.El. Gohary, O.D.El. Monayeri, Urban Environ. Engng. **9**, 82 (2015)
2. G. Zhen, X. Lua, H. Katoc, Y. Zhaod, Y.Y. Lia, Renew Sustain Energy Review **69**, 559 (2017)
3. A.T. Hendriks, G. Zeeman, Bioresource Technol. **100**, 8 (2009)
4. M. L. Christensen, K.Keiding, H. Nielsen, M.K. Jørgensen, Water Res **82** (2015)
5. M. Carlsson, A. Lagerkvist, F. Morgan-Sagastume, Waste Manag **32**, 1634 (2012)
6. S. Myszograj, Pol J Environ Stud **2**, 166 (2010)
7. U. Kepp, I. Machenbach, N. Weisz, O.E. Solheim, Water Sci Tech **42**, 89 (2000)
8. J. Górka, M. Cimochoicz-Rybicka, M. Kryłów, E3S Web of Conferences **30**, 02006 <https://doi.org/10.1051/e3sconf/20183002006> (2018)
9. Y.Y. Li, T. Noike, Water Sci Tech **26**, 857 (1992)
10. R.A. Fisher, S.J. Swanwick, Water Pollut. Contr. **71**, 255 (1971)
11. G. Elbing, A. Dünnebeil, Korrespondenz Abwasser **46**, 538 (1999)
12. J. A. Müller, Water Sci Tech **44**, 121 (2001)
13. R Core Team, *R: A language and environment for statistical computing* (R Foundation for Statistical Computing, Vienna, Austria, URL <https://www.R-project.org/>, 2017)
14. S. Tanaka, T. Kobayashi, K. Kamiyama, M.L.N. Bildan, Water Sci Tech **35**, 209 (1997)
15. M.J. Lindstrom, D.M. Bates, Biometrics **46**, 673 (1990)
16. M. Climent, I. Ferrer, M. Mar Baeza, A. Artola, F. Vazquez and X. Font, Chem. Eng. Journal **133**, 335 (2007)
17. J. Kim, J Bioscience and Bioeng **95**, 271 (2003)
18. A. Valo, H. Carre`re, J. Delgene`s, J Chem. Technol. Biotechnol. **79**, 1197 (2004)
19. S. Graja, J. Chauzy, P. Fernandes, L. Patria, D. Cretenot D., Water Sci. Tech. **52**, 267 (2005)
20. M. Carballa, F. Omil, M. Lema, Proceedings (10th World Congress Montréal, Canada, 2004)