Comparison of Various Kinetic Models for Batch Biodegradation of Leachate from Tobacco Waste Composting

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This paper presents kinetic analyses of biodegradation of organic matter from leachate which is produced during the composting process of tobacco waste. Four different kinetic models were applied to the data. The kinetic analysis was performed with traditional Monod model, modified Monod model with endogenous metabolism, Haldane model and Haldane model which is expanded with endogenous metabolic consumption and called Endo-Haldane model. Kinetic parameters for each model were determined using differential analysis and the Nelder-Mead method of nonlinear regression. The lowest deviations and very good matches with experimental data were achieved using Endo-Haldane model. This fact pointed out that this model best described the process of biodegradation of leachate from tobacco waste composting. This is due to fact that this model incorporates both, effects of inhibition and endogenous metabolism.

Keywords: activated sludge, biodegradation, kinetic parameters, leachate, tobacco waste

Tobacco waste appears in different steps of tobacco processing after harvest as well as in the course of manufacturing of some tobacco products such as cigarettes. Due to increasingly affluent lifestyles, continuing growth of tobacco products was observed. The consequence of increased manufacture of tobacco products is raising the level of various tobacco wastes. The biggest problem concerning these wastes is the presence of toxic and hazardous compounds, especially nicotine [1; 2].

Uncontrolled disposal of tobacco waste can become a serious threat for the environment and is also a hazard to people's health. Increasingly stringent environmental regulations require the processing of waste and wastewater before disposal or release into the environment.

Total elimination of nicotine, as well as stabilization of product can be achieved by aerobic composting of tobacco waste. Whilst composting technology has successfully facilitated the diversion of organic waste from landfill, and can produce a very high quality end-product, it is associated with some potential environmental hazards, one of which is the production of compost leachate. Nicotine is highly soluble in water, therefore there is a serious risk that when stored, nicotine may be leached from the wastes and may migrate into ground waters and surface waters [3-6].

Over many years, conventional biological treatments and physical-chemical methods have been considered the most appropriate technologies for manipulation and management of high strength effluents like landfill leachate. Activated sludge process is commonly used for biodegrading organic contaminants in wastewater using a mixed population of microorganisms at relatively high concentration in an aerobic environment, which can degrade organic compounds to carbon dioxide and sludge under aerobic conditions [7-9]. There are many mathematical models which can be applied for activated sludge wastewater treatment. Mathematical modelling can be helpful for understanding the behaviour of biological process and predicting the concentrations of organic matter in the system.

The purpose of this work was to study the kinetic properties of the activated sludge process by removal of the pollutant organic matter, represented by the decrease in the chemical oxygen demand (COD). Various kinetic models have been successfully applied including Monod model, modified Monod model with endogenous metabolism, Endo- Haldane model and Endo-Haldane model with inhibition in order to evaluate the kinetic parameters of each model.

Experimental part

Material and methods

Activated sludge and leachate

The activated sludge sample was taken from the Wastewater Treatment Plant (WWTP) in Zagreb, ZOV, Croatia. The sludge sample from WWTP is collected from aeration tank, centrifuged (Sigma 3K15, Germany) at 5,411 ×g for 10 min and 0°C. The initial activated sludge concentration was 5.8 g dm^{-3}.

The leachate used in this research is one of products of composting the tobacco solid waste in closed thermally insulated column reactor of 25 dm^3 following the method of Briški et al. [10]. At the end of experimental period, after 16 days, 716 cm^3 of leachate was produced and COD value was 14128 mg dm^{-3}. For the set of experiments, the original leachate was diluted with tap water to the desired initial concentrations of 500, 100, 1500 mg dm^{-3} and marked as S1, S2, S3, respectively.

Aerobic biodegradation

Batch biodegradation experiments were conducted in 500 cm^3 conical flasks using 250 cm^3 of diluted leachate and inoculated with 15 g of the centrifuged activated sludge. Samples were taken every 6 h for determination of

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chemical oxygen demand (COD), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MVLSS). All experiments were performed at $25\pm2^{\circ}$C and were maintained in aerobic conditions agitated on a rotary shaker at 160 rpm for 48 h.

Analytical methods

Mixed liquor suspended solids (MLSS), as well as mixed liquor volatile suspended solids (MVLSS) were determined gravimetrically and the chemical oxygen demand (COD) was determined by means of the dichromate method using Standard Methods [11]. All determinations were averages of duplicate samples.

Kinetic analysis

The modeling was conducted using the assumption that COD (*S*) represents the rate limiting substrate and MLVSS (*X*) represents the amount of the active biomass. Performing substrate and biomass balance on the batch reactor at constant volume yields the equation for biomass growth rate, r_X which is well described by the following first order kinetic equation [12-14]:

$$r_X = \frac{dX}{dt} = \mu X \tag{1}$$

where μ is the specific growth rate of biomass. Simultaneously to the production of the biomass, the substrate is degraded, and the equation for substrate degradation rate, r_S is:

$$r_S = -\frac{dS}{dt} = \frac{\mu X}{Y} \tag{2}$$

wherein *S* is the limiting substrate concentration, *X* is the biomass concentration, and *Y* is the overall yield coefficient. Substrate degradation rate can also be expressed by the following equation:

$$r_S = -\frac{dS}{dt} = qX \tag{3}$$

where *q* is the specific substrate degradation rate, single parameter which characterizes the degradation process.

Rearranging eqs. (1)–(3), the equation for biomass growth rate can be presented according to the expressions:

$$r_X = qXY \tag{4}$$

$$r_X = r_S Y \tag{5}$$

There are several expressions which relate the specific rates (μ and *q*) to the substrate concentration. In bioprocess modeling, substrate limitation, which may occur during the process, may be modelled by various kinetic models. Due to its reliability and simplicity, Monod model, modified Monod model with endogenous metabolism, Haldane model and Endo-Haldane model are commonly used.

The most frequently applied is the Monod model, which describes the dynamic behaviour of the process, i.e. shows relationship between specific growth rate of biomass and limiting nutrient (substrate):

$$\mu = \frac{\mu_{\max} S}{Ks + S} \tag{6}$$

This model is the traditional Monod model wherein μ_{max} is maximum specific growth rate, and *Ks* is Monod saturation constant (i.e. substrate concentration at half μ_{max}).

At the end of the process, when the most of organic matter from leachate is removed, due to lack of substrate some weaker cell population becomes food for the healthier one. Due to biomass decay, endogenous or decay coefficient, k_d must be incorporated in the original Monod model. This coefficient correspondents to endogenous metabolism which involve reactions in cells that consume cell substances [12;15;16]:

$$\mu = \frac{\mu_{\max} S}{Ks + S} - k_d \tag{7}$$

When a substrate inhibits its own biodegradation, the Monod model is inadequate and must be modified by incorporating with the inhibition constant K_i [16]:

$$\mu = \frac{\mu_{\max} S}{Ks + S + S^2 / K_i} \tag{8}$$

This is Haldane model which takes into account inhibition constant (*Ki*), which is a measure of sensitivity to inhibition by inhibitory substances. However, some authors proposed that decline in cell population, i.e. biomass decay, after the complete consumption of substrate should be taken into account [12; 17]. Therefore, after attaching coefficient of microbial decay k_d in express of Haldane model equation takes the following form:

$$\mu = \frac{\mu_{\max} S}{Ks + S + S^2 / K_i} - k_d \tag{9}$$

This is modified Haldane model, which will be referred to as the Endo-Haldane model hereafter. This model is frequently used, because of its ability to account for the effect of inhibition at high concentration, and of cell death and/or maintenance metabolism at low concentration. The inhibition constant corresponds to the highest substrate concentration at which the specific growth rate equals one-half of the maximum specific growth rate without inhibition [12; 16].

Results and discussions

Concentrations of activated sludge

In a biological treatment process, sludge concentration is an important factor to ensure biological treatment ability. A sufficient sludge concentration will ensure good performance in pollutant removal [18]. The mixed liquor suspended solids (MLSS) is an indirect measure of sludge concentration which is common used to characterize the biological mass in the activated sludge. The Mixed Liquor Volatile Suspended Solids (MLVSS) is a measure of the amount of volatile suspended solids found in a sample of mixed liquor suspended solids (MLSS). The volatile solids concentration of MLSS is approximately equal to the amount of microorganisms in leachate, therefore can be used to determine whether there are enough microorganisms present to digest the sludge [15].

Figure 1 shows changes of MLVSS concentrations compared to the initials concentrations of leachate. The concentration of MLVSS is directly connected with the amount of viable sludge. The initial MLVSS concentration in all conducted experiments was 4.28 g dm^{-3}. During 36 h MLVSS was gradually increased up to 4.36 g dm^{-3}, 4.47 g dm^{-3}, and 4.56 g dm^{-3} for S1 – S3, respectively. After that due to the reduction of the amount of organic matter and

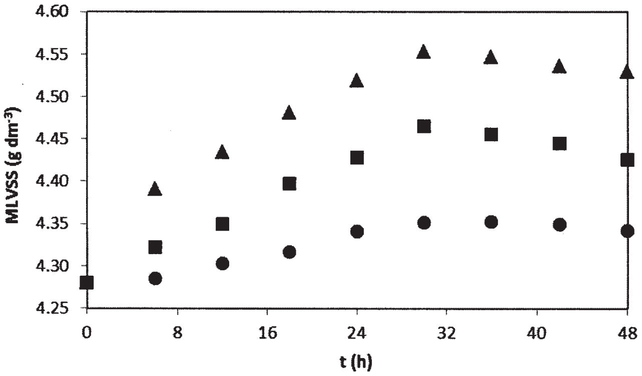

Fig. 1. Changes of volatile solid concentrations in activated sludge during biological treatment at starting COD concentrations of 500 mg dm^{-3} (•), 1000 mg dm^{-3} (■), and 1500 mg dm^{-3} (▲)

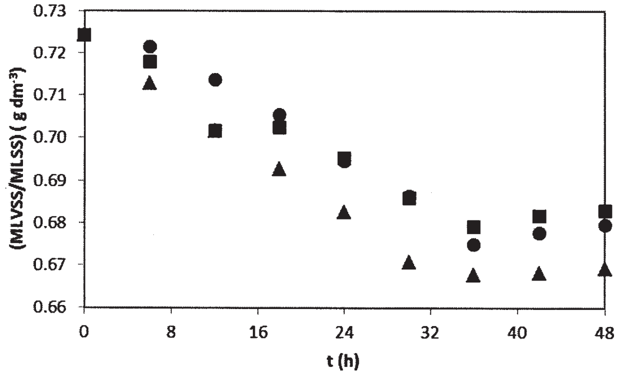

Fig. 2. Variations of MLVSS/MLSS ratio during biological treatment at starting COD concentrations of 500 mg dm^{-3} (•), 1000 mg dm^{-3} (■), and 1500 mg dm^{-3} (▲)

the activity of the microbial population concentration of MLVSS had slightly decreased for all conducted experiments. The ratio of MLVSS/MLSS indicates a change in biomass concentration.

Figure 2 shows that MLVSS/MLSS ratio varied only slightly and ranged in optimal limits (0.668 – 0.724) over the whole experimental period for S1 – S3, respectively. These results indicate that biomass was adapted to the processing conditions.

Model selection and parameter estimation

Based on the values obtained for COD removal, kinetic analysis was performed using four different models. COD removal is one of the main indicators, which is used to assess the efficiency of degradation process of organic pollutant from leachate. From figure 3 is obviously that COD values were decreased for each concentration compared to the initial value of the untreated leachate. The decrease in initial concentration of leachate resulted in the increase in efficiency of biodegradation up to a value of 55.8 , 57.9 and 61.2 % for S1 – S3, respectively.

Figue 3 shows comparison of Monod and Endo-Haldane model with experimental data. It is obvious that the Endo-Haldane model gives a better correlation than the Monod model.

The kinetic analysis was performed using traditional Monod model, modified Monod model with endogenous metabolism, Haldane classic model and Endo-Haldane model which considers effects of inhibition and biomass decay. Due to mathematical similarity between Monod and Haldane model, as well as between modified Monod model and Endo-Haldane model, figure 3 shows only comparison of experimental data with values obtained using Monod model and Endo-Haldane model. Kinetic parameters were

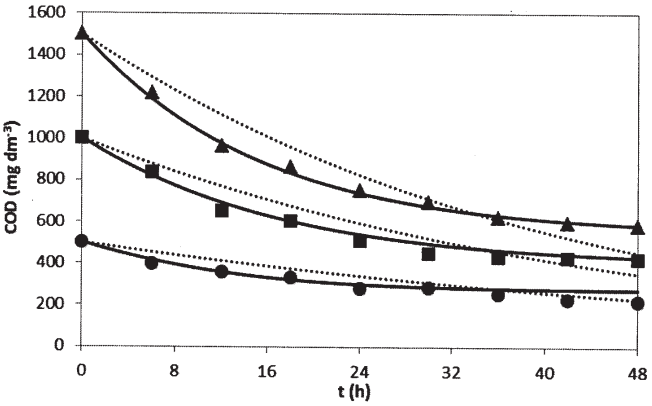

Fig. 3. COD removal from leachates: S1 (•), S2 (■), S3 (▲) during 48 h and comparison of experimental data with values obtained using Monod model (···) and Endo-Haldane model (——).

estimated in all of the afforementioned models and for all conducted experiments, from S1 to S3, respectively. The kinetic parameters in equations (eqs. 6-9) were estimated using differential analysis and the Nelder – Mead method of nonlinear regression. Differential equations (eqs. 6-9) describing the system, were numerically solved using Runge-Kutta method. According to the procedure as described, table 1 shows values calculated for kinetic parameters evaluated in kinetic models, as well as values obtained for sum of squares of residuals and for statistical Fisher-Snedecor F-test .

Model comparison

Criteria for the choice of the objective function were the sum of squares of residuals and Fisher-Snedecor F-test between the calculated and average experimental values of the COD (*S*). Values obtained for the sum of squares of residuals do not give enough information because different models can have a different number of parameters [19]. Therefore, data fits obtained by using the various models were compared statistically by the use of the Fisher-Snedecor F-test.

Fisher-Snedecor F-test

Fisher-Snedecor F-test enables the comparison of experimental data with values obtained using aforementioned differential types of models. The statistic F-test was conducted using the assumption that the null hypothesis is [20]:

$$H_0: s_1^2 = s_2^2$$

and the alternative hypothesis is:

$$H_1: s_1^2 \neq s_2^2$$

where s_1^2 and s_2^2 are variances that we were comparing. The test statistic for comparing variances is given by the formula[21]:

$$F = \frac{s_1^2}{s_2^2}$$

If the two functions have the same variances, then s_1^2 and s_2^2 , variances of the samples that are drawn from them, are close in value and F is close to 1. On the other hand, if those variances are very different, then s_1^2 and s_2^2 tend to be very different. Using the assumption that s_1^2 is the smaller variance than s_2^2 , the values of F-test ranged between 0 and 1. Therefore, if F is close to 1, the evidence

Table 1
EVALUATED KINETIC PARAMETERS FOR ALL CONDUCTED EXPERIMENTS FROM S1 TO S3

Model	μ_{max} (h^{-1})			K_S (mg dm^{-3})			K_i*10^2 (mg dm^{-3})			k_d *10^2 (h^{-1})			S.E. *10^2 (-)			F test (-)		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
Monod model	0.75	0.63	0.78	36.8	24.6	28.9	-	-	-	-	-	-	1.68	2.03	1.91	0.69	0.77	0.76
Monod model with endogenous metabolism	1.12	1.54	2.07	25.5	24.2	32.8	-	-	-	0.78	2.3	3.23	0.99	0.72	0.54	0.89	0.97	0.99
Haldane model	0.98	0.97	1.11	49.2	40.1	26.3	7.63	9.26	6.93	-	-	-	1.67	2.02	2.92	0.70	0.73	0.55
Endo-Haldane model	1.95	2.95	3.61	36.8	41.1	40.8	10.1	18.8	18.4	1.02	2.63	4.6	0.96	0.69	0.53	0.94	0.98	1.00

is in favour of the null hypothesis that two variances are equal.

From the table 1 it can be seen that models (7) and (9) describe the process of degradation of organic matter from leachate much better than models (6) and (8). These models take into account endogenous metabolism and substrate inhibitions term. At the end of the process, there is an evident reduction of the amount of organic matter, and the activity of the aerobic microbes. A particular cell population becomes food for the healthier one what causes the changes in microbial community and inhibition of the process. Also, effect of inhibition may be caused by high initial concentration of leachate, because initial trend of substrate consumption is not possible to predict. Therefore, the inhibition of substrate degradation, as well as endogenous metabolism should also be taken into account.

Also, it can be confirmed by the fact that the presence of the microbial endogenous metabolism allows the models to predict constant substrate concentration attained at the end of the process, whereas the classical Monod model, which does not have this term, predicts zero concentration at the end of the process. The presence of endogenous metabolism and substrate inhibitions term in Endo-Haldane model enables it to predict the initial trend of substrate consumption rate of both high and low concentration runs and constant substrate concentration attained at the end of process, so this model gives the best fit to the experimental data [12].

The values obtained for kinetic constants in this study, except of the values of $_{max}$ are very close to the values of kinetic coefficients which are reported in literature [22]. The maximum specific growth rate (μ_{max}) should be in the range of 0.131-0.363 h^{-1} for mixed microbial cultures. The divergence of these values has been attributed to cell type and culture environments [23]. The values obtained for the kinetic constant for endogenous metabolism are similar to the value reported by Beltran-Heredia et al. [24]. Values of K_s, were in the range which corresponds to typical values for activated sludge process [25] which means that the microorganisms had a good affinity to substrate degradation.

Results obtained statistically by F-test and standard error confirm that Endo-Haldane model gives the best fits with experimental data.

Conclusions

The analysis of the biodegradation of organic matter present in leachate and the comparison of experimental values with values obtained by four differential mathematical models were studied. COD removal efficiency ranging between 55.8 % and 61.2 % was achieved after 48 h. These results confirmed that the leachate was biologically treatable. Based on the fit of experimental data to each model and values obtained for standard error, as well as values obtained by statistic F-test it was found that Endo – Haldane model, which incorporates inhibition effect and endogenous metabolism, provides the best description of the degradation process in all experimental runs from S1 to S3, respectively. However, the Monod model with endogenous metabolism also described the process very well with negligible differences between obtained values for kinetic parameters, F-test and standard errors. The results of kinetic studies can be useful in operating the existing activated sludge system efficiency and can be applied in novel design studies for industrial purposes.

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Symbols

COD - chemical oxygen demand, mg dm^{-3}
MLSS - mixed liquor suspended solids, g dm^{-3}
MLVSS - mixed liquor volatile suspended solids , g dm^{-3}
K_S - substrate saturation constant, mg dm^{-3}
K_i - inhibition constant, mg dm^{-3}
k_d- kinetic constant for endogenous metabolism, h^{-1}
r_S - substrate degradation rate, mg dm^{-3} h^{-1}
r_X - biomass growth rate, g dm^{-3} h^{-1}
S - substrate concentration, mg dm^{-3}
X - biomass concentration, g dm^{-3}
Y - overall yield coefficient, g g^{-1}
t - time, h
μ - specific growth rate of biomass, h^{-1}
μ_{max} maximum specific growth rate, h^{-1}

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