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DEGRADATION OF LEACHATE FROM TOBACCO DUST BY ACTIVATED SLUDGE PROCESS

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Abstract

Treatment of tobacco dust represents an important problem because of high concentrations of organic compounds, expressed as COD concentration. This research investigated an aerobic biodegradation of leachate from tobacco dust with high concentrations of COD. Experiments were conducted by activated sludge process in batch conditions with different initial concentrations of leachate and different initial concentrations of activated sludge (3.0, 6.0 g dm^{-3}) during 7 hours. Experiments were called Exp. 1 and Exp. 2 with respect to initial concentrations of activated sludge. Values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. Biokinetic analysis was conducted according to the Monod model. This model gives very good fits to experimental data, accompanied by a high correlation coefficient (R^2).

Keywords: *tobacco waste, leachate, aerobic biodegradation, kinetic study*

1. INTRODUCTION

Increasingly affluent lifestyles, continuing industrial and commercial growth in many countries around the world in the past decade has been accompanied by rapid increases in both the municipal and industrial solid waste. The classification of industrial wastes of organic origin includes tobacco wastes, which are generated during different processes of the tobacco and cigarette production cycle [1,2].

Tobacco waste and dust appear in different steps of tobacco processing after harvest as well as in the course of manufacturing of some tobacco products such as cigarettes. The consequence of increase manufacture of tobacco products is raising level of various tobacco wastes. These waste products are resold, recirculated, compacted, or put in landfills.[3,4]. The biggest problem concerning these wastes is the presence of toxic compounds. Investigations carried out showed that the most important sources of these toxic contaminants are nicotine, flavouring chemicals containing glycogen and alcohol, absorbable organic halogens (AOX), and pesticides from tobacco leaves [5]. The nicotine contains high concentration of toxic compounds, and the powdery structure which cannot be recycled. Nicotine is highly soluble in water; therefore the toxic compound, nicotine can be transferred from the solid phase to an aqueous solution through efficient percolation. It may also be leached from the wastes and may permeate into ground waters and surface waters [1,2,6,7].

The main characteristic of tobacco solid wastes and leachate, beside their toxicity is their low moisture content. Due to of this problem it is desirable to apply biological or thermal process during the treatment of these wastes. Biological treatment is flexible, reliable, and high cost-effectiveness, which is commonly used for treatment of tobacco solid wastes and leachate.

This study aims to investigate the aerobic biodegradation of organic pollutants of leachate from tobacco dust in batch bioreactor, and evaluate biokinetic parameters using the Monod model.

2. ELABORATION

2.1. Experimental

The activated sludge sample was taken from the Wastewater Treatment Plant 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. Initial concentrations of activated sludge were 3.0 and 6.0 g dm^{-3}. The leachate used in the research was prepared from tobacco dust, Hrvatski duhani d.d., Virovitica according to European standard of EN 12457-4:2002 [8]. The leachate sample that was obtained from the tobacco waste contained high COD, 40000 mg dm^{-3}. For the set of experiments, the leachate sample was diluted to initial concentrations of 500, 1000, 1500, 3000, 5000 mg dm^{-3}.

Batch biodegradation experiments were conducted in 500 cm^3 conical flasks using 250 cm^3 of diluted leachate and inoculated with 7.5 g (Exp. 1) and 15 g (Exp. 2) of the centrifuged activated sludge. Samples were taken every hour for determination of chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MVLSS), pH value and dissolved oxygen (DO), and for microscopic investigation. All experiments were performed at 25±2°C and were maintained in aerobic conditions agitated on a rotary shaker at 160 rpm for 7 hours.

Mixed liquor suspended solids (MLSS) and 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 (APHA, 1998). Dissolved oxygen (DO) and pH values were measured with an oxygen meter and pH meter (WTW Multi 340i, Germany). All determinations were averages of duplicate samples.

The morphology of the activated sludge was investigated by light microscopy. Samples of activated sludge were monitored under a light microscope (Olympus BX50, Olympus Optical Co. Ltd., Japan, with Olympus DP 10 camera). A drop of mixed liquor was carefully deposited on a glass slide and covered with a cover slip before being observed through the microscope.

2.2. Results and Discussion

2.2.1. Pollutant removal performances

Legal regulation dictates that wastewater and leachate must be treated before it can be discharged. Activated sludge process has been widely applied to treat wastewater and leachate due to its advantages including low running cost and high degradation efficiency [1].

Chemical oxygen demand (COD) value is used to evaluate the organic strength of leachate. A biodegradation was conducted for leachate originated from tobacco waste. This leachate sample contained very high COD, 40000 mg dm^{-3}. Therefore it was diluted to initial concentrations of 500, 1000, 1500, 3000, 5000 mg dm^{-3} marked by from S1 to S5, respectively. The total removal reached in every experiment is calculated and shown in Fig.1.

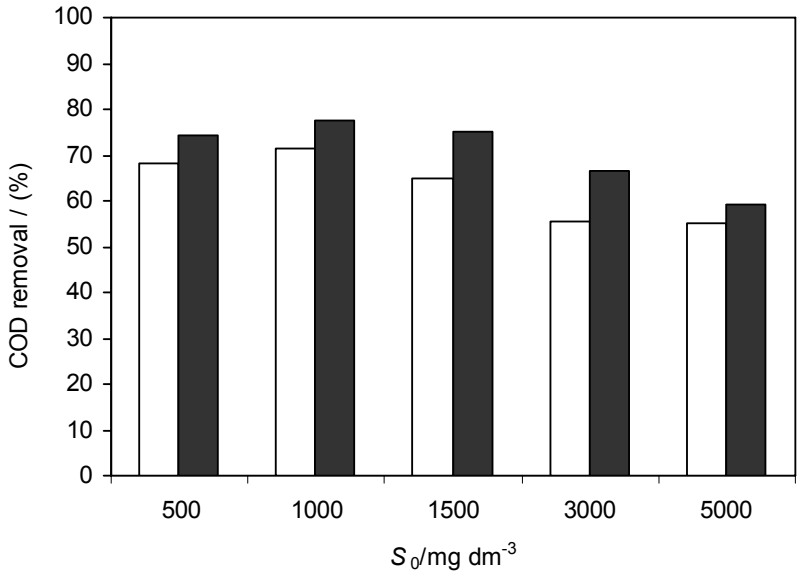

Figure 1. Efficiency of biodegradation of leachate from tobacco dust at different starting concentrations of substrate for Exp. 1 (□) and Exp. 2 (■).

For the series varying initial substrate concentration, values of COD concentration decreased continuously with reaction time. Values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. These results demonstrated that the leachate was biologically treatable. Results show that efficiency is the best for leachate with initial concentration of 1000 mg dm^{-3}. In this case COD was reduced to 71.3 % for Exp. 1 and 77.7 % for Exp. 2. It can be explained that the ratio of biomass and substrate was optimal and suitable, what enables the production of a quality effluent with a high value of performance degradation. We can see that efficiency of biodegradation was gradually decreased for samples with highest initial concentration for Exp. 1 and Exp. 2, respectively. It

can be explained by the fact that ratio of biomass and substrate was not optimal. Therefore, there is possibility that an inappropriate ratio biomass and substrate causes inhibition of substrate degradation at higher initial concentration of leachate.

2.2.2. Response of the control variables

In biological treatment process, use of activated sludge is an effective way of treating leachate with high concentrations of organic compounds. 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 and better effluent quality [9]. The mixed liquor suspended solids (MLSS) present a mixture of activated sludge and suspend solids from leachate. It should be noted that the MLSS consists of organic and inorganic matter, as well as microorganisms, and other inert suspended matter. Therefore, the MLSS is an indirect measure of total biomass [10]. Initial MLSS concentrations were 3.11 and 6.0 g dm^{-3} for conducted experiments marked as Exp. 1 and Exp. 2, respectively.

For both experiments during 7 hours concentration of MLSS was lightly and gradually increased. By increase of initial concentrations of substrate from S1 to S5, values of MLSS increased up to 26.13 % for Exp. 1. In the Exp. 2, values of concentrations of MLSS show significantly smaller increase with respect to starting concentrations of 6.0 g $dm^{-3}$and increased up by only 6.98 %.

The mixed liquor volatile suspended solid (MLVSS) represents the amount of organic or volatile suspended solids in sample of MLSS. This volatile portion is used as a measure or indication of the presence of microorganisms. The presence of microorganisms plays important role in the process of biodegradation. Therefore, the ratio of MLVSS/MLSS can be used to determine whether there are enough microorganisms present to digest the sludge and biodegradation. Variations in ratio of MLVSS/MLSS indicate a change in amount of biomass share

Table 1. Results of the control variables obtained in the Exp. 1.

Exp. 1	MLVSS/MLSS	pH	DO, mg dm^{-3}
S1	0.714 ± 0.03	8.15 ± 0.16	5.91 ± 1.08
S2	0.716 ± 0.02	7.99 ± 0.12	4.36 ± 1.16
S3	0.719 ± 0.02	7.94 ± 0.10	3.62 ± 0.92
S4	0.726 ± 0.02	7.85 ± 0.10	1.60 ± 0.90
S5	0.732 ± 0.03	7l.76 ± 0.13	0.57 ± 0.25

Table 2. Results of the control variables obtained in the Exp. 2.

Exp. 2	MLVSS/MLSS	pH	DO, mg dm^{-3}
S1	0.717 ± 0.02	7.92 ± 0.19	4.27 ± 1.30
S2	0.719 ± 0.01	7.89 ± 0.19	3.88 ± 1.22
S3	0.723 ± 0.01	7.85 ± 0.18	2.88 ± 1.34
S4	0.748 ± 0.02	7.77 ± 0.21	1.05 ± 1.01
S5	0.725 ± 0.03	7.69 ± 0.24	0.31 ± 0.02

Table 1. and 2. show that the values obtained for ratio of MLVSS/MLSS were almost constant and range in limits from 0.714 to 0.732 for Exp. 1 and from 0.717 to 0.725 for Exp. 2. These results show that there were no significant changes in the amount of viable sludge. The environmental factor that influences rates and limits microbial growth and thus the process of biodegradation is the pH value. The pH value lightly decreased by increasing initial concentration of leachate and ranged in optimal limits (7.76 – 8.15) and (7.69 – 7.92) for Exp. 1 and Exp. 2, respectively. These values correspond to the biological activity of sludge [12].

In aerobic bioprocesses, the control of the dissolved oxygen level plays an important role. The dissolved oxygen concentration in the activated sludge process should be sufficiently high to supply enough oxygen to microorganisms in the sludge in order for the organic matter to be degraded by them

[11]. Average values of DO concentration (Tab.1. and Tab.2.) decreased by increasing initial concentration of leachate. We can see that values of the average concentration of dissolved oxygen are significantly low at higher concentration of leachate in both conducted experiments. It is due to the fact that at higher initial concentration of leachate a lot more oxygen is necessary for substrate degradation [13].

2.2.3. Biokinetic analysis

Microbial degradation is generally defined as the biologically catalyzed reduction in chemical complexity. In the natural environment, conditions for biodegradation are very complex and the rate and extent of biodegradation depend on the chemical, physical and biological factors that may be different for different ecosystems. Although microbial processes are very complex, individual process incidences or groups of these incidences can be represented by model [12].

Most analyses with regards to biokinetic in wastewater treatment processes were done on the assumption that the reaction follows Monod kinetics or first-order reactions. This model defines the functional dependence of the specific growth rate and biomass concentration [12, 13], equation (1):

$$\mu = \mu_{\max} \cdot S / (K_s + S) \tag{1}$$

where in μ (h^{-1}) is the specific growth rate, μ_{max} (h^{-1}) is maximum specific growth rate, S (mg COD dm^{-3}) is the limiting substrate concentration and K_s (mg dm^{-3}) is substrate saturation constant (i.e. substrate concentration at half μ_{max}).

Microbial growth occurs as a consequence of the process of biodegradation by removing substrates as described by equations (2) and (3)

$$r_x = X_v / dt = \mu X_v \tag{2}$$

$$r_s = dS / dt = q_s X_v \tag{3}$$

where r_s (mg COD dm^{-3} h^{-1}) is substrate degradation rate, r_x (mg MLVSS dm^{-3} h^{-1}) is biomass growth rate, X_v (mg MLVSS dm^{-3}) is biomass concentration, q_s (mg COD (mg MLVSS)$^{-1}$ h^{-1}) is specific substrate degradation rate and t (h) is time.

The concentration of the substrate is usually reduced by growth of microorganisms, therefore r_s (mg COD dm^{-3} h^{-1}) is well described by equation (4):

$$r_s = \mu_{\max} X_v S / Y(K_s + S) \tag{4}$$

where Y (mg MLVSS (mg COD)$^{-1}$) is overall yield coefficient.

Real biomass yield per substrate, $Y_{x/s}$, and specific substrate degradation rate, q_s can be calculated directly from experimental data from the following equations (5) and (6):

$$Y_{x/s} = (X_v - X_{v0}) / (S_0 - S_i) \tag{5}$$

$$q_s = ((S_0 - S_i) / (t_0 - t_i)) / (X_v - X_{v0}) \tag{6}$$

According to this procedure, Tables 3. and Tables 4. show values of kinetic results in the aerobic degradation process and biokinetic parameters evaluated by kinetic model. Model parameters were estimated by non-linear regression analysis using least - squares method implemented in MS Excel software. Numerical values of model parameters were obtained by fitting the model to experimental data using MS Solver software. The optimization method was conducted according to GRG2 (Generalized Reduced Gradient) which is integral part of MS Solver software. Differential equations of the model are solved numerically by Runge Kutta 4 algorithm. A set of optimal parameters of the model were used for the process simulations. The residual error was defined as the sum of squares of the differences between the experimental and calculated data.

Tab 3. shows the values obtained for parameters ($Y_{x/s}$ and q_s) in the experiment according to Eq. (5) and Eq. (6). The growth yield coefficient, $Y_{x/s}$, is defined as increase in biomass which results from the utilization of amount of substrate. Mean values obtained for growth yield coefficient $Y_{x/s}$ (mg MLVSS (mg COD)$^{-1}$) are in the range from 0.355 to 0.393 mg mg^{-1} and from 0.189 to 0.242 mg mg^{-1} in conducted experiments marked as Exp. 1 and Exp. 2. These values show good match with expected values for the activated sludge process. Data obtained for specific substrate degradation rates, q_s (mg COD (mg

MLVSS)$^{-1}$ h^{-1}) are very close with other values proposed in the literature for the aerobic biodegradation of different wastewater [14].

Table 3. Mean values of kinetic results in the aerobic degradation process.

S_0 (mg dm^{-3})	Exp. 1		Exp. 2	
	$Y_{x/s}$ (mg mg^{-1})	q_s (mg mg^{-1} h^{-1})	$Y_{x/s}$ (mg mg^{-1})	q_s (mg mg^{-1} h^{-1})
500	0.355±0.12	0.027±0.04	0.189±0.06	0.022±0.02
1000	0.369±0.07	0.074±0.06	0.193±0.06	0.048±0.04
1500	0.391±0.04	0.094±0.07	0.213±0.08	0.065±0.06
3000	0.389±0.02	0.144±0.04	0.235±0.10	0.106±0.10
5000	0.393±0.07	0.217±0.09	0.242±0.09	0.120±0.20

Table 4. Biokinetic parameters.

Biokinetic parameters	Exp. 1	Exp. 2
μ_{max} (h^{-1})	0.088	0.052
K_s (mg dm^{-3})	4241	3168
Y (mg mg^{-1})	0.400	0.257

Applying a non-linear regression analysis to the experimental results were estimated biokinetic parameters according to Eq. (4). Tab. 4. shows the values of obtained results. Comparison of model and experimental results are shown Fig. 2. and Fig. 3. for Exp. 1 and Exp. 2. A good arrangement of the experimental points around a straight line confirms the agreement with the proposed model.

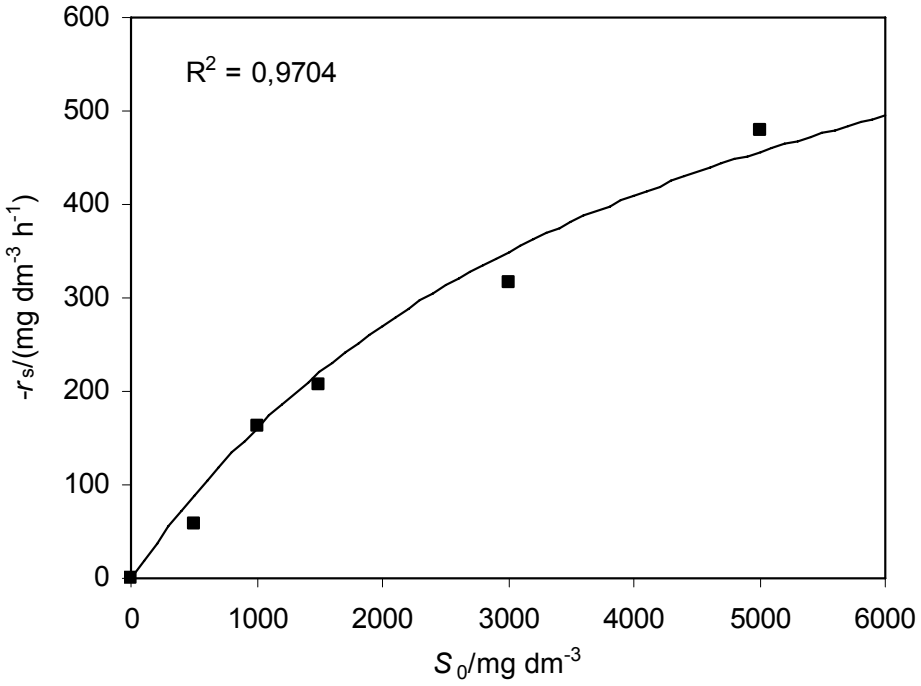

Figure 2. Influence of initial COD on substrate degradation rate for Exp. 1, (■) experimental data, and (—) model.

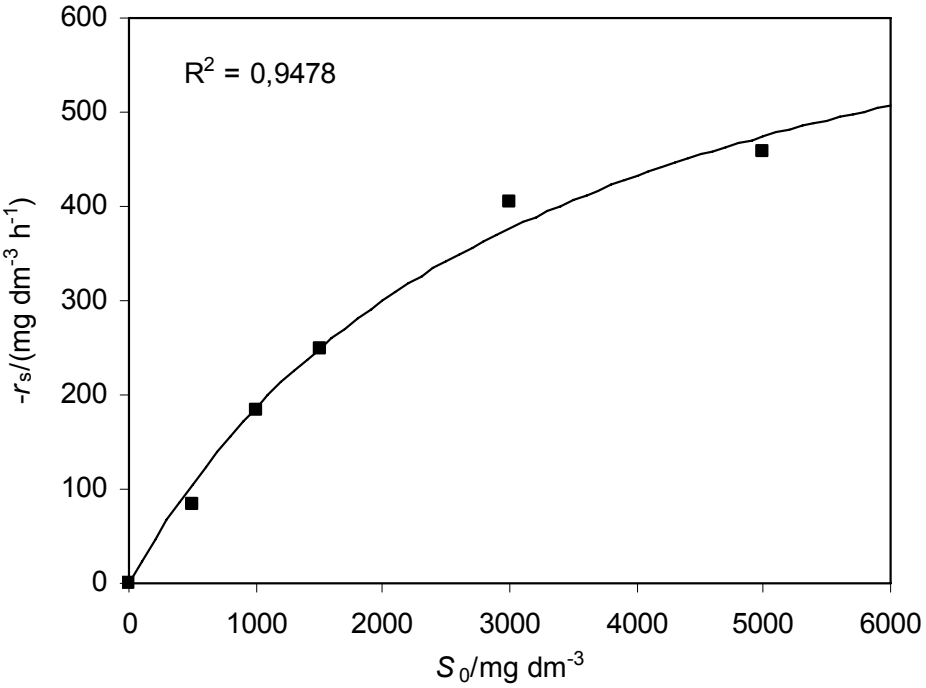

Figure 3. Influence of initial COD on substrate degradation rate for Exp. 2, (■) experimental data, and (—) model.

Fig.2. shows fit of calculated values obtained from model and experimental results for Exp. 1. As can be seen substrate degradation rate, r_s (mg COD dm^{-3} h^{-1}), is increased when initial substrate concentration also increases, as could be expected.

Also, Fig. 3. show fit of calculated values obtained from model and experimental results for Exp. 2. We can see that Exp. 1 shows insignificantly better match to experimental data than Exp. 2. These results demonstrated that the applied Monod model describes well the dynamics of the process accompanied by a high regression coefficient (R^2 = 0.9704 for Exp. 1, and R^2 = 0.9704 for Exp. 2)

2.2.4. Microscopical Examination

MLSS were regularly monitored to adjust the sludge concentration to a preset level. In order to describe the morphology of the activated sludge, microscopic investigation was conducted. The morphological properties of sludge were characterized by flocs [15, 16]. Flocs present in water play an important part in all issues related to water quality and treatment. Small sludge flocs can provide a favourable environment for enhancement of mass transfer, thus enabling the system to show a higher organic removal rate [16].

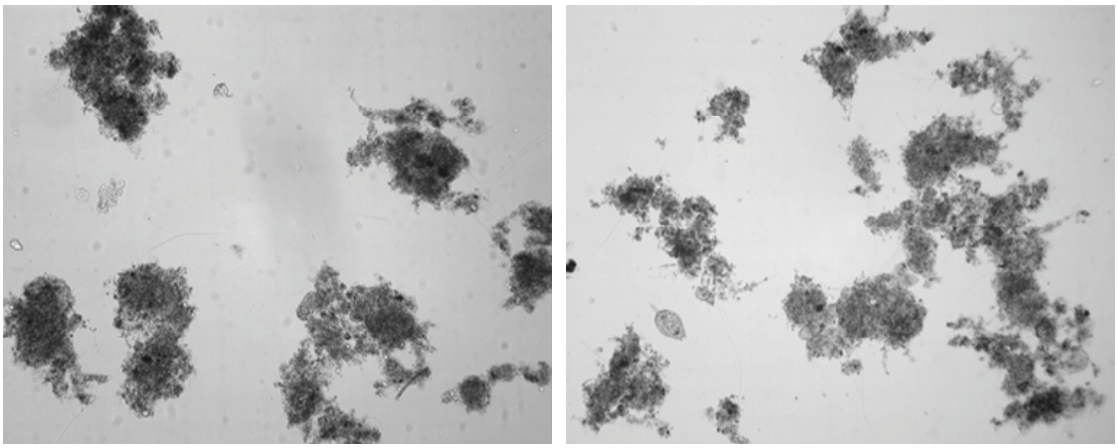

Fig.4. Microphotographs of activated sludge flocs in batch conditions for Exp. 1 and Exp. 2, respectively: left- at the start of the experiment and right- at the end of the experiment (100× magnification)

The results of microscopically examination are shown in Fig. 4.These figures show form of the flocs at the beginning and at the end of the process. The flocs at the beginning of the process shown in Fig.4.-left are characterized by regular formed flocs which enables producing a high quality effluent. We can see, also that flocs at the beginning of the process were significantly more compact than flocs at the end of the process. This can be explained by the fact that microorganisms at the end of process were not sufficiently supplied by substrate which is necessary for growth and maintenance of flocs.

3. CONCLUSIONS

The obtained results have shown biodegradability of leachate from tobacco dust. The values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. The ratio of MLVSS/MLSS and pH value were almost constant and ranged in optimal limits during the whole experimental period for Exp. 1 and Exp. 2, respectively. These results correspond to biological activity of activated sludge. Average values of DO concentrations decreased by increasing initial concentrations from 5.91 to 0.57mg dm^{-3} and from 4.27 to 0.31 mg dm^{-3} for Exp. 1 and Exp. 2, respectively. Obtained results show that microorganisms consumed most oxygen to oxidize most of available organic matter, and that the maximum oxygen consumption was in experiments with higher concentrations of substrate. The application of Monod model describes well the reaction kinetics for conducted experiments. Good fits to experimental data and high regression coefficient (R^2) pointed out that biological treatment of leachate from tobacco dust was successfully conducted.

Nomenclature

COD	chemical oxygen demand	mg dm^{-3}
DO	dissolved oxygen concentration	mg dm^{-3}
K_s	substrate saturation constant	mg dm^{-3}
MLSS	mixed liquor suspended solids	g dm^{-3}
MLVSS	mixed liquor volatile suspended solids	g dm^{-3}
q_s	specific substrate degradation rate	mg mg^{-1} 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}
t	time	h
X_v	biomass concentration	mg dm^{-3}
Y	overall yield coefficient	mg mg^{-1}
$Y_{x/s}$	growth yield coefficient	g g^{-1}
μ	specific growth rate of biomass	h^{-1}
μ_{max}	maximum specific growth rate of biomass	h^{-1}

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