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#### EFFICIENCY OF BIOLOGICAL LEACHATE TREATMENT FROM TOBACCO WASTE

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#### Abstract

In this study an aerobic treatment of leachate from tobacco waste using activated sludge under batch conditions was carried out. In experiments, pH value, dissolved oxygen, chemical oxygen demand (COD), and suspended solids have been monitored. Leachate treatment was conducted with different initial concentrations of leachate from 500 to 5000 mg dm<sup>-3</sup> and initial concentrations of activated sludge from 1.84 to 6.62 g dm<sup>-3</sup> during 96 hours. Leachate treatment efficiency was 80.0 - 99.8 % for Experiment A, 88.0 - 91.5 % for Experiment B, 87.0 - 92.0 % for Experiment C, 84.0 - 96.0 % for Experiment D, and 81.0 - 95.0 % for Experiment E in respect to initial COD concentrations. *Keywords: biological treatment, leachate, tobacco waste* 

#### **1. INTRODUCTION**

Concern about environmental protection has increased over the years from a global viewpoint. During cigarette manufacturing large quantities of tobacco waste are produced annually and its disposal is a serious ecological problem. Treatment of tobacco waste represents a major problem because of high concentrations of toxic compounds [1-3].

Leachate is a complex wastewater with considerable variation in both quality and quantity. Leachate consists of many different organic and inorganic compounds that may be either dissolved or suspended and which are biodegradable and non-biodegradable. Increasingly stringent environmental regulations require the processing of waste and wastewater before disposal or release into the environment. The removal of organic material based on chemical oxygen demand (COD), biochemical oxygen demand (BOD) and BOD/COD ratio from leachate is the usual prerequisite before discharging the leachates into natural waters. The knowledge of these specific parameters may help to select suitable treatment processes for the lowering of organic matter present in leachate [4-6].

During many years, conventional biological treatments and physical-chemical methods have been considered as the most appropriate technologies for manipulation and management of high strength effluents like landfill leachate. Due to its reliability and simplicity, biological treatment is commonly used for leachate treatment. In recent years, biological processes have been considered to be a cost-effective and environmentally sustainable alternative for the treatment of such wastewaters. Aerobic biological processes based on suspended-growth biomass, such as aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR) have been widely studied and adopted. SBR technology has become an attractive option for tobacco wastewater treatment. Activated sludge is a process for biodegrading organic contaminants in wastewater using a mixed population of microorganisms at relatively high concentration in an aerobic environment, which can degrade organics compounds to carbon dioxide and sludge under aerobic conditions [7-9].

The aim of this work was to study the efficiency of biodegradation of organic pollutants of leachate from tobacco waste under batch conditions.

#### **2. ELABORATION**

#### **2.1.** Experimental

Batch biodegradation experiments were conducted in 500 cm<sup>3</sup> conical flasks using 250 cm<sup>3</sup> of diluted leachate and inoculated with 15.0 g, 12.5 g, 11.3 g, 7.5 g, and 3.8 g of the centrifuged activated sludge for experiments A-E, respectively. Samples were taken every 24 h for determination of chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MVLSS), pH value and dissolved oxygen (DO). At the beginning of the experiment COD and

biochemical oxygen demand (BOD<sub>5</sub>) of original leachate medium were measured. All experiments were performed at  $25\pm2^{\circ}$ C and were maintained in aerobic conditions agitated on a rotary shaker at 160 rpm for 96 hours.

The activated sludge sample was taken from the Wastewater Treatment Plant in Zagreb, ZOV, Croatia. The sludge sample from WWTP was collected from aeration tank, centrifuged (Sigma 3K15, Germany) at 5,411 ×g for 10 min and 0 °C. Experiments were performed under different activated sludge concentration levels,  $X_0$ , in the range of 1.84-6.62 g dm<sup>-3</sup> (MLSS).

The leachate used in the research was prepared from solid sample of the tobacco waste, Hrvatski duhani d.d., Virovitica, Croatia according to European standard of EN 12457-4:2002 [10]. The starting concentration of prepared leachate was around 34430 mg dm<sup>-3</sup> COD, and value of BOD<sub>5</sub> was of approximately 18572 mg dm<sup>-3</sup>. For the set of experiments, the leachate sample was diluted to initial concentrations,  $S_0$ , of 500, 1000, 1500, 3000, and 5000 mg dm<sup>-3</sup> (COD), and marked as  $S_1 - S_5$ , respectively.

MLSS and MVLSS were determined gravimetrically, and BOD, COD measured according to APHA standards [11]. 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. Sludge samples were collected from the bioreactor and 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

One of the principle aims of present day wastewater treatment is the removal of organic carbon (COD) from wastewaters. COD and biochemical oxygen demand (BOD<sub>5</sub>) are two of the most common generic indices used to assess aquatic organic pollution. BOD<sub>5</sub> is often used to evaluate the biodegradable fraction, and COD the total organic pollution load of waters contaminated by reductive pollutants. The biodegradability criterion for wastewater is the ratio of BOD/COD, which was about 0.54 in the leachate medium. The relatively higher values of ratio indicate pollution of the leachate by biodegradable matter. Biological processes have been shown to be very effective in removing organic matter from leachates when the BOD/COD ratio has a high value (>0.5) [5,12,13].

Exp. #	MLSS (mg dm <sup>-3</sup> )	MLVSS/MLSS	рН (-)	DO (mg dm <sup>-3</sup> )
А	$6.62 \pm 0.02$	$0.716\pm0.02$	$7.75\pm0.10$	$3.24\pm0.76$
В	$5.04 \pm 0.04$	$0.620\pm0.03$	$7.79\pm0.08$	$3.42 \pm 0.81$
С	$4.06 \pm 0.04$	$0.654\pm0.02$	$8.04\pm0.24$	$5.21\pm0.84$
D	3.11±0.01	$0.689\pm0.04$	$8.14\pm0.22$	$4.38 \pm 1.31$
Е	1.84±0.06	$0.687\pm0.03$	$8.17\pm0.27$	$5.36 \pm 1.00$

Table 1. Experimental results in the aerobic biodegradation process.

Experimental results in the aerobic biodegradation process are shown in Tabel 1. In a biological treatment process, sludge concentration is an important factor to ensure biological treatment ability. The mixed liquor suspended solids (MLSS) were used to characterize the biological mass in the activated sludge. The initial MLSS concentration in experiments was 6.62-1.84 g dm<sup>-3</sup> for Exp. A - E, respectively. Tabel 1 shows the ratio of MLVSS/MLSS changes in the bioreactor over the experimental period. This value was in the range 0.620-0.716, almost constant over the whole experimental period. That indicated no obvious accumulation of inorganic matter in the bioreactor [14].

The important environmental factor that affects to activity of microorganisms in activated sludge is pH value. The optimum pH value for biological process of wastewater treatment is in the range 6.0 - 9.0, therefore it is an optimum range of the most economic purification processes [15-17]. Tabel 1 shows that pH values for conducted experiments varied only slightly and ranged in optimal limits of 7.75 to 8.17. There has been an increase in pH values in all experiments, A through E. The increase in pH value was most probably caused by oxidative effect of biodegradation process [5].

In aerobic bioprocesses, available dissolved oxygen for the growth and maintenance of microorganisms is often the most critical parameter which limits the effectiveness of the process. Therefore the control of DO plays an important role in the process of biodegradation. The concentration of DO in bioreactor affects on the behaviour and activity of microorganisms living in the activated sludge. Some authors suggest that concentration of DO should be in the range of 0.5 to 5.0 mg  $O_2 \text{ dm}^{-3}$  [18]. The values that are within the concentration gradient of 0.5 to 5.0 mg  $O_2 \text{ dm}^{-3}$  are considered sufficiently high to supply enough oxygen to microorganisms for biodegradation.

For series of conducted experiments, designated from A to E, concentrations of dissolved oxygen were in the range 3.24 - 5.36 mg dm<sup>-3</sup>. We can see that values for Exp. C and Exp. E slightly deviated from optimal values but not significantly, so they did not affect the quality of the sludge and the efficiency of biodegradation. Therefore, we can say that all obtained values correspond to values proposed in the literature for the aerobic biodegradation of wastewater.

The biokinetic parameters were calculated using the concentration range of 500 - 5000 mg dm<sup>-3</sup> for Exp. A and Exp. D, during the experimental period of 96 hours. The most important is the cell metabolism synthesis phase (parameter  $Y_{x/s}$ ) with production of new cells (MLVSS). The food-to-microorganism ratio (F/M) is controlled by the rate of activated sludge wasting [13].

Table 2. Weah values of blokmetic parameters in the actoble blodegradation proces					
	$S_0$	Exp. A		Exp. D	
$(mg dm^{-3})$		$Y_{x/s}$	F/M	$Y_{x/s}$	F/M
	(ing unit )	$(mg mg^{-1})$	$(mg mg^{-1} h^{-1})$	$(mg mg^{-1})$	$(mg mg^{-1} h^{-1})$
	500	0.326±0.06	$0.003 \pm 0.01$	$0.401 \pm 0.06$	$0.004 \pm 0.01$
	1000	0.334±0.05	$0.007 \pm 0.01$	$0.385 \pm 0.08$	$0.011 \pm 0.01$
	1500	0.351±0.07	$0.010 \pm 0.02$	$0.378 \pm 0.04$	$0.019{\pm}0.03$
	3000	$0.360 \pm 0.07$	$0.018 \pm 0.04$	$0.403 \pm 0.03$	$0.031 \pm 0.06$
	5000	0.347±0.06	$0.021 \pm 0.07$	0.396±0.03	$0.042 \pm 0.08$

Table 2. Mean values of biokinetic parameters in the aerobic biodegradation process.

Results obtained from batch biodegradation experiments A and D are shown in Tabel 2. Growth yield is defined as increase in biomass which results from the utilization of amount of substrate. The growth yield coefficient,  $Y_{X/S}$ , is defined as the ratio of maximum mass of cells formed to the mass of substrate utilized. The overall biomass yield *Y*, at time  $t_{end}$  is  $Y_{X/S} = MLVSS_{max} - MLVSS_0 / COD_0 - COD_{max}$  where MLVSS<sub>0</sub> and MLVSS<sub>max</sub> are biomass concentration at the start of the experiment and maximum biomass concentration reached throughout the experiments. Similarly, COD<sub>0</sub> and COD<sub>min</sub> are corresponding substrate concentrations [19]. Mean values of  $Y_{X/S}$  varied between 0.326-0.347 g MLVSS (g COD)<sup>-1</sup> and 0.401 -0.396 g MLVSS (g COD)<sup>-1</sup> from 500 to 5000 mg dm<sup>-3</sup> in experiment A and D, respectively. For the conventional activated sludge process for treating wastewater, growth yield is normally in the range 0.25–0.4 g MLVSS (g COD)<sup>-1</sup> [14].

The food to microorganism (F/M) ratio tells us something about growth and cell condition. In biological wastewater treatment process, F/M is calculated through dividing the amount of treated organic material per unit time by the amount of microorganisms [20]. As can be seen from Table 2, in this study the values of F/M ratio increased by increasing initial concentration of substrate from 0.003 to 0.021 g COD (g MLVSS)<sup>-1</sup> h<sup>-1</sup> for Exp. A and 0.004 to 0.042 g COD (g MLVSS)<sup>-1</sup> h<sup>-1</sup> for Exp. D. In experiment A value of F/M ratio was lower than in experiment D. Low F/M ratio equals little substrate per unit biomass, which leads to competition among microorganisms and results in reduction of the net sludge production. This is in accordance with the maintenance which demands that biomass growth slows down with decreasing nutrient supply [19].

The biological component of the activated sludge system is comprised of microorganisms. A light microscope was used to examine the microorganism population of the activated sludge system. The diversity of the microbial community in activated sludge is very large. Protozoa are a useful biological indicator of the condition of the activated sludge. The hallmark of a well-operated, stable activated-sludge system is the existence of large numbers of highly evolved protozoa in the biological mass [13,21]. The results of microscopic examination are shown in Fig. 1.

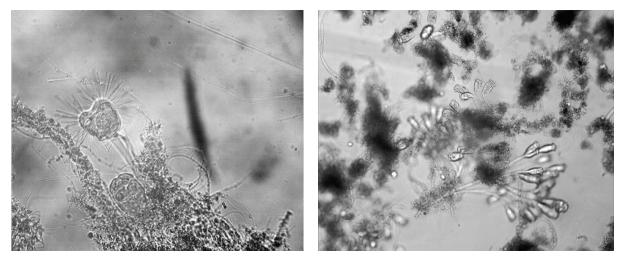


Figure 1. Microphotographs of protozoa from the batch reactor in the aerobic biodegradation process.

These microscopic images show some species of Protozoa which were present over the course of the experiment. Presence of protozoa populations provides evaluation of sludge quality and biodegradation ability. Protozoa are significant predators of bacteria which play a key role in the degradation processes. Therefore we can say that the presence of protozoa in activated sludge indicates a good quality of activated sludge, as well as the good performance of the process of biodegradation [17,22].

Biological treatment methods are extensively applied for the treatment of different type of wastewater and leachate. Conventional activated sludge process is suboptimal for tobacco wastewater treatment. The main purpose of this process is a removal of organic pollution from wastewater by microorganisms that are in activated sludge. The organic pollution of the leachate is expressed as COD which represents the amount of oxygen consumed by the organic compounds and inorganic matter which were oxidized in water by microorganisms [5,23,24].

Exp.		COD removal (%)				
#	$S_1$	$S_2$	$S_3$	$S_4$	$S_5$	
А	$80.0\pm0.16$	$99.8\pm0.32$	$89.3\pm0.67$	$90.8 \pm 1.40$	$90.4\pm2.67$	
В	$87.8\pm0.10$	$91.5\pm0.13$	$91.1\pm0.38$	$91.3 \pm 1.13$	$91.3\pm3.47$	
С	$87.0\pm0.13$	$90.9\pm0.20$	$91.8\pm0.43$	$91.5 \pm 1.15$	$90.6\pm3.67$	
D	$83.8\pm0.23$	$91.7\pm0.65$	$90.0\pm0.76$	$93.4 \pm 2.13$	$95.9{\pm}3.98$	
Е	$81.0\pm0.16$	$89.5\pm0.44$	$87.3\pm0.54$	$93.3 \pm 1.85$	$95.1\pm4.78$	

Table 3. Efficiency of biodegradation of the leachate expressed as COD removal

After the biological treatment, the efficiency of COD removal was approximately 80 - 99%, as shown in Table 3, considering all the experiments. The highest COD removal (99.8 %) was obtained with 6 g dm<sup>-3</sup> of activated sludge concentration (Exp. A). These values are very similar to other values proposed in the literature for an aerobic biodegradation of tobacco wastewater [23].

#### **3. CONCLUSIONS**

The obtained results have shown efficiency of biodegradation of organic pollutants of leachate from tobacco waste under batch conditions. The ratio of MLVSS/MLSS was in the range 0.620–0.716. These values show that biomass maintained throughout the experiments. The pH values and DO were about 7.96 and between 3.24 to 5.36 g dm<sup>-3</sup>. Values of pH and DO were in the optimal range for biodegradation processes. Mean value of  $Y_{X/S}$  was approximately 0.368 g MLVSS (g COD)<sup>-1</sup>. The F/M ratio was between 0.003 and 0.042 g COD (g MLSS) <sup>-1</sup> d<sup>-1</sup>. In all conducted experiments efficiency of COD removal was high and ranged from 80.0 to 99.9%.

#### Nomenclature

COD	chemical oxygen demand	$mg dm^{-3}$
$\text{COD}_0$	initial substrate concentration	mg dm <sup>-3</sup>
COD <sub>min</sub>	minimum substrate concentration	$mg dm^{-3}$
DO	dissolved oxygen concentration	mg dm <sup>-3</sup>
F/M	food to microorganism ratio	$g g^{-1} d^{-1}$
MLSS	mixed liquor suspended solids	g dm <sup>-3</sup>
MLVSS	mixed liquor volatile suspended solids	g dm <sup>-3</sup>
$MLVSS_0$	initial biomass concentration	g dm <sup>-3</sup>
MLVSS <sub>max</sub>	maximum biomass concentration	g dm <sup>-3</sup>
$Y_{\rm X/S}$	growth yield coefficient	$g g^{-1}$
$S_{0/i}$	initial substrate concentration	mg dm <sup>-3</sup>

#### REFERENCES

- I.J. Buerge, M. Kahle, H.R. Buser, M.D. Muller, T. Poiger, Nicotine derivatives in wastewater and surface waters: application as chemical markers for domestic wastewater. Environ. Sci. Technol. 42 (2008), 6354–6360.
- [2] M. Wang, G. Yang, H. Mina, Z. Lv, X. Jiab, Bioaugmentation with the nicotine-degrading bacterium *Pseudomonas* sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms Water Res. 43 (2009) 4187–4196.
- [3] F. Briški, Z. Gomzi, N. Horgas, M.Vuković, Aerobic composting of tobacco solid waste. Acta Chim. Slov., 50 (2003) 715-729.
- [4] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, J. Hazard. Mater. 171 (2009) 54–56.
- [5] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150 (2008), 468–493.
- [6] M.C. Tomei, M.C. Annesini, S.Bussoletti, 4-Nitrophenol biodegradation in a sequencing batch reactor: kinetic study and effect of filling time. Water Res. 38 (2004), 375–384.
- [7] E. Celis, P. Elefsiniotis, N. Singhal, Biodegradation of agricultural herbicides in sequencing batch reactors under aerobic and anaerobic conditions. Water Res. 42 (2008) 3218–3224.
- [8] B. Bae, E. Jung, Y. Kim, H. Shin, Treatment of landfill leachate using activated sludge process and electron-beam radiation, Water Res. 33 (1999) 2669–2673.
- [9] J. Dollerer, P.A. Wilderer, Biological treatment of leachates from hazardous waste landfills using SBBR technology. Water Sci. Technol. 34 (1996) 437–453.
- [10] EN 12457-4:2002, Characterization of waste Leaching; Compliance test for leaching of granular waste materials and sludges - Part 4: One-stage batch test at a liquid to solids ratio of 10 l/kg for materials with particle size below 10 (without or with size reduction), European Committee for Standardization.
- [11] APHA (1998). Standard methods for examination of water and wastewater, 20th Edition. APHA, Washington DC, USA.
- [12] L.K. Wang, N.C. Pereira, Y.-T. Hung, Biological treatment processes, Humana Press, New York, 2009, pp. 207-278.
- [13] G. Bitton, Wastewater Microbiology, John Wiley & Sons, New York, 1994.
- [14] X. Huang, P. Gui, Y. Qian, Effect of sludge retention time on microbial behaviour in a submerged membrane bioreactor, Process Biochem. 36 (2001) 1001–1006.
- [15] W. Wesley Eckenfelder, Industrial Water Pollution Controll, 3rd edition, McGraw Hill Environ. Engineering Series, New York, 2000. str. 109, 124, 186, 417, 462.
- [16] S. Zheng, Y. Zhang, T. Tong, C. Cui, J. Sun, Dominance of yeast in activated sludge under acidic pH and high organic loading, Biochemical Engineering Journal 52 (2010) 282-288.
- [17] S.F. Yang, X.Y. Li, H.Q. Yu, Formation and characterisation of fungal and bacterial granules under different feeding alkalinity and pH conditions, Process Biochemistry. 43 (2008) 8–14.
- [18] B. Holenda, E. Domokos, A. Redey, J. Fazakas, Dissolved oxygen control of the activated sludge wastewater treatment process using model predictive control, Computer and Chemical Engeineering 32 (2008) 1270-1278.

- [19] E. Sahinkaya, F.B. Dilek, Biodegradation of 4-chlorophenol byacclimated and unacclimated activated sludge-Evaluation of biokinetic coefficients, Environ. Res. 99 (2005) 243-252.
- [20] S.-H. Yoon, Important operational parameters of membrane bioreactor-sludge disintegration (MBR-SD) system for zero excess sludge production, Water Res. 37(2003) 1921–1931.
- [21] C.A. Papadimitriou, A. Papatheodoulou, V. Takavakoglou, A. Zdragas, P. Samaras, G.P. Sakellaropoulos, M. Lazaridou, G. Zalidis, Investigation of protozoa as indicators of wastewater treatment efficiency in constructed wetlands, Desalination. 250 (2010) 378-382.
- [22] M. Vuković, F. Briški, M. Matošić, I. Mijatović, Analysis of the activated sludge process in an MBR under starvation conditions, Chem. Eng. Technol. 29 (2006) 357-363.
- [23] M. Wang, G. Yang, H. Min, Z. Lv, X. Jia, Bioaugmentation with the nicotine-degrading bacterium Pseudomonas sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms, Water research. 43 (2009) 4187-4196.
- [24] F. Kargi, Y. Pamukoglu, Aerobic biological treatment of pre-treated landfill leachate by fed-batch operation. Enzyme Microb. Tech. 33 (2003) 588-595.