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MODELLING OF THE AIR PURIFICATION FROM VOLATILE ORGANIC COMPOUNDS IN A TRICKLE-BED BIOREACTOR

MODELOWANIE PROCESU OCZYSZCZANIA POWIETRZA Z LOTNYCH ZWIĄZKÓW ORGANICZNYCH W BIOREAKTORZE STRUŻKOWYM

Abstract: The biodegradation of styrene by bacterial strain *Pseudomonas* sp. E-93486, coming from VTT Culture Collection (Finland), was studied. The kinetic experiments with the presence of styrene as the only carbon and energy source were performed both in batch and continuous cultures at optimal environmental conditions for the growth of the tested strain (pH = 7 and 30ºC). The Haldane inhibitory model was found to be the best to fit the kinetic data, and the estimated kinetic equation parameters were: μ_m = 0.119 h^{-1}; K_s = 5.984 $g \cdot m^{-3}$, K_i = 156.6 $g \cdot m^{-3}$. The experiments conducted in a chemostat at various dilution rate (D = 0.035-0.1 h^{-1}) made it possible to determine the value of the coefficient for maintenance metabolism (m_d = 0.0165 h^{-1}) and the maximum yield coefficient value ((Y_{XS})$_{max}$ = 0.913). The determined complete model of growth of E-93486 strain in the presence of styrene was verified by comparison of the computed and obtained in batch experiments profiles of changes in biomass and styrene concentrations. Next the tested strain was immobilized on the packing of a pilot-scale trickle-bed bioreactor operating at co-current down-flow of gas (air contaminated by styrene) and liquid (mineral solution) phases. The effect of inlet styrene concentration on its degradation was studied for initial concentration in the air changing in the range of 0.2-1 $g \cdot m^{-3}$. The recirculation rate of liquid medium was 8 $m^3 h^{-1}$ whereas the gas flow rate was changed in the range 50-150 $m^3 \cdot h^{-1}$. The conversion degree depended on operational parameters and changed in subsequent experiments in the range of 75-95%.

Keywords: styrene, kinetics, trickle-bed bioreactor

Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere in large quantities from chemical and petrochemical industries. As styrene is included in this category, the economic and effective removal of styrene from waste gas and waste water from chemical plants is needed. It is released into the environmental during the manufacturing and application of its isomers including polystyrene, styrene-butadiene rubber, acrylonitrile and copolymers resins. Styrene is employed in the chemical industry as a starting material for synthetic polymers as well as a solvent in the polymer processing industry and is, therefore, present in many industrial effluents. The world production capacity of styrene amounts to about 32.5 Tg and constantly increase, on average by 2-3% a year. Such common and quantitatively big styrene consumption considerably affects its emission into the atmosphere, estimated at 25 Gg a year. In general, the concentration of styrene in industrial waste gases may reach 1 $g \cdot m^{-3}$ [1], and average range varies between 0.15 and 0.4 $g \cdot m^{-3}$ [2]. Styrene has been listed among the 189 hazardous and toxic atmospheric contaminants under Clean Air Act Amendments [3].

Chronic exposure to styrene in humans results in a variety of discomforts such as mucous membrane and eye irritations, headache, fatigue, weakness, depression, central

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nervous system dysfunction, hearing loss, and peripheral neuropathy [4]. Styrene is suspected to be potentially carcinogenic, mainly through pulmonary and percutaneous arterial absorption (solvents generally modify the cytoplasmic and external membranes). Styrene oxide, which is an oxidation product of the side chain and the major *in vivo* metabolite of styrene, may also have an immunomodulatory effect on workers exposed to gaseous emissions in an industrial setting [5]. Therefore, before discharge to the environment, both the liquid and gaseous effluents of industrial complexes should undergo an appropriate treatment to decrease the concentration of styrene to below toxic level [4, 6].

Many different methods have been used for the treatment of styrene laden waste gas streams. The use of physicochemical processes such as catalytic and thermal oxidations, wet scrubbing and activated carbon adsorption, incurs high capital and operating costs and usually results in the production of secondary effluents and does not always reduce the pollutant concentration in the air or wastewater to acceptable levels. Therefore, the biotreatment has proven to be an effective and economical technology with minimal energy requirements and low waste production among the different air pollution control techniques for reducing VOCs and odors in air.

Biotreatment provides significant advantages over conventional techniques, such as adsorption, condensation, activated carbon adsorption, and thermal and catalytic oxidation, in terms of large air volumes and low gaseous pollutant concentrations.

Biofiltration is the cost effective and reliable option in treating VOCs emitted from processes with large off-gas volume but low concentration of pollutants [7]. Three types of biofiltration such as biofilter (BF), trickle-bed bioreactor (TBB) and bioscrubber (BS) have been developed for the treatment of waste gases. A trickle-bed bioreactor (TBB) consists of an inert packed bed on which microbial biofilm grows and a nutrient-trickling system. TBBs often exhibit higher treatment performance than BFs, because more active biomass can be accumulated and reactor operation conditions can be effectively controlled. One drawback of TBBs is excess biomass accumulation on a packed bed. This produces a high pressure drop and reduces removal efficiency of the biofilter [8].

Before proceeding with the research associated with the determination of efficiency of the process of biopurification of the air from styrene, the optimal environmental conditions for growth of the selected microorganisms were examined and next kinetic equation describing both the rate of the growth of the tested strain and styrene degradation were developed. The worked out kinetic model was verified basing on our own experimental data-base, obtained in batch experiments. Than the series of experiments of biopurification of air from styrene was carried out in pilot scale trickle- bed bioreactor. The aim of the experiments was to determine the range of the operational parameters for which maximum elimination capacity was achieved.

Materials and methods

Microorganisms

The culture of gram-negative bacteria used in this study, coming from VTT Culture Collection (Finland), showed 97% homology with *Pseudomonas putida* and 97% with *Pseudomonas stutzeri* from 16SrDNA analysis. The strain, marked as E-93486, was isolated from the activated sludge enriched with styrene [9]. Proliferation of the cells and

pre-incubation with styrene in the concentration of 90 g·m^{-3} was performed as described previously [10].

Analytical methods

The concentration of biomass was determined by measuring the optical density (OD) of the fluid culture (λ = 550 nm). Next, the suspension absorbance was converted into grams of dry mass of microorganisms according to the calibration curve. Styrene concentration was determined by gas chromatography using Varian 3800 (USA) chromatograph as described previously [10].

Results and discusion

Effect of temperature and pH on E-93486 growth

Before proceeding with the research associated with styrene biodegradation the effect of pH and temperature on the growth of the selected strain was examined. Pure cultures of *Pseudomonas* sp. E-93486 were inoculated into a triplicate sets of 500 cm^3 Erlenmeyer flasks containing LB medium. Part of them was adjusted to pH of 5, 6, 7 or 8 and incubated in a shaker at 30°C, another part was adjusted to pH 7 and incubated at 21, 25, 30 or 35ºC (Fig. 1). Optimal environmental conditions for the growth of tested strain were pH = 7 and 30°C and all experiments presented below were performed maintaining these parameters.

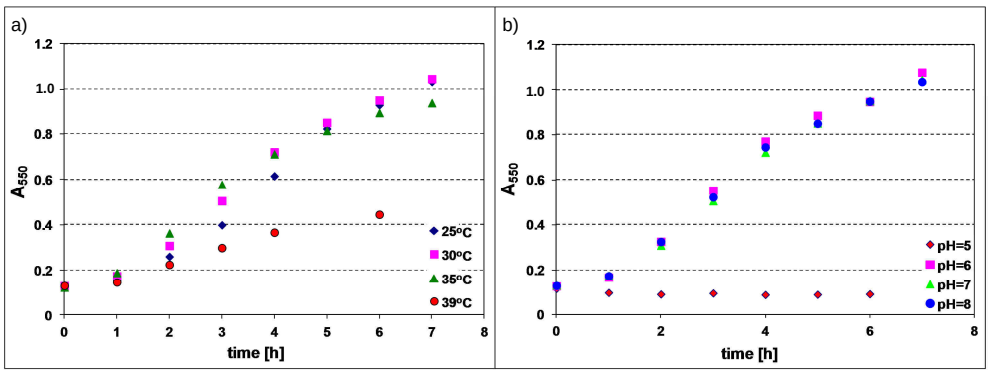

Fig. 1. The rate of growth of E-93486 strain at different temperatures (a) and pH values (b)

Kinetic experiments

The kinetic model parameters are usually obtained from batch experiments by observing the biomass growth rate with time at a different initial concentration of substrate. Microbial growth tests in the presence of styrene as the sole carbon and energy source were conducted in Biostat B fermenter (Sartorius, USA), with working volume of 2.7 dm^3, operating both in batch and continuous mode. Batch experiments were carried out for initial styrene concentration in the liquid phase changing in the range 5-90 g·m^{-3}. A ln$X$ = $f(t)$ graph (X [g·m^{-3}] is concentration of biomass, t [h] is time) was plotted for every experimental point. In the exponential growth phase, the dependence is a straight line of

slope (μ_{net}). The compiled data-base made it possible to choose kinetic model and to determine its constants. The Haldane inhibitory model:

$$\mu_{net} = \frac{\mu_m S_l}{K_S + S_l + \frac{S_l^2}{K_i}} \tag{1}$$

was found to be the best to fit the kinetic data. In equation (1) μ_{net} [h^{-1}] is net specific growth rate, S_l [$g \cdot m^{-3}$] is concentration of styrene in the liquid phase, μ_m [h^{-1}] is the model parameter, K_S and K_i are the half saturation constant [$g \cdot m^{-3}$] and substrate inhibition constant [$g \cdot m^{-3}$], respectively.

The kinetic equation parameters were estimated basing on the own database using the least-square error method with the help of NLReg programme, and they were: $\mu_m = 0.119\ h^{-1}$; $K_s = 5.984\ g \cdot m^{-3}$, $K_i = 156.6\ g \cdot m^{-3}$.

The developed equation with a mean relative error:

$$e_Y = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\mu_{exp,i} - \mu_{calc,i}}{\mu_{exp,i}} \right| \cdot 100\% \tag{2}$$

not exceeding 5.5% approximates the experimental data. In Eq. (2) subscripts *exp* and *calc* denote experimental and calculated values, respectively.

The conducted experiments made it possible also to determine the value of the observed biomass yield coefficient ($(Y_{XS})_{obs} = 0.72$) (Fig. 2).

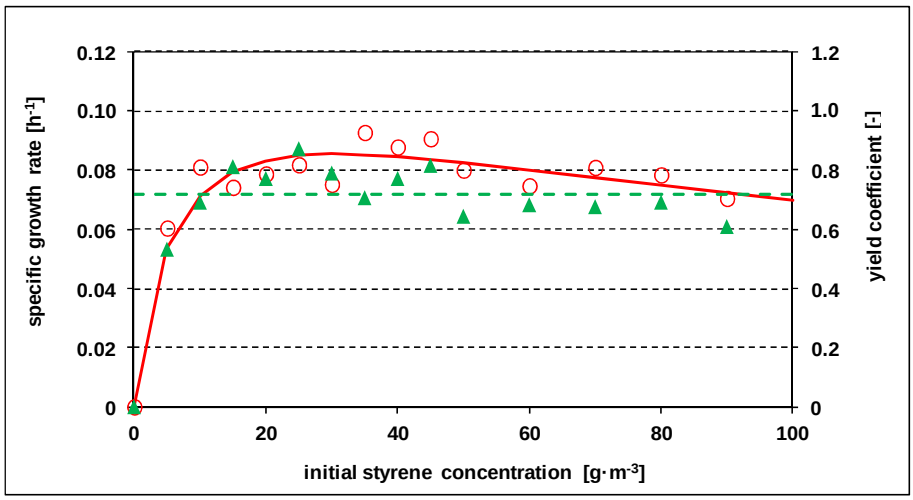

Fig. 2. Specific growth rate (circles) and observed yield coefficient (triangles) as a function of initial styrene concentration (solid line correspond to the model prediction)

The experiments conducted in a chemostat at various dilution rate (D = 0.035-0.1 h^{-1}) enabled us to determine the value of the coefficient for maintenance metabolism (m_d = 0.0165 h^{-1}) and the maximum yield coefficient value ($(Y_{XS})_{max}$ = 0.913). The determined complete model of growth of E-93486 strain in the presence of styrene allows

to calculate the profiles of the changes of biomass and growth substrate concentrations in the periodic cultures. For this purpose the system of differential equations must be solved:

$$\frac{dX}{dt} = \left(\frac{0.119 S_l X}{5.984 + S_l + \frac{S_l^2}{156.6}}\right)\left(1 - exp\left(-\frac{t}{t_l}\right)\right) \tag{3}$$

$$-\frac{dS_l}{dt} = \frac{1}{0.913}\left(\frac{dX}{dt}\right) + 0.0165 \cdot X \tag{4}$$

where X is the concentration of cells, S_l is concentration of styrene in the liquid phase, t and t_l are time and duration of lag phase, respectively; the last term on the right hand side of Eq. (3) considers the existence of an adaptation phase of duration t_l. The above system of equations with the initial condition:

$$\text{when } t = 0, \text{ than } X = X_0 \text{ and } S_l = S_{l0} \tag{5}$$

was solved by Runge-Kutta 4th order method.

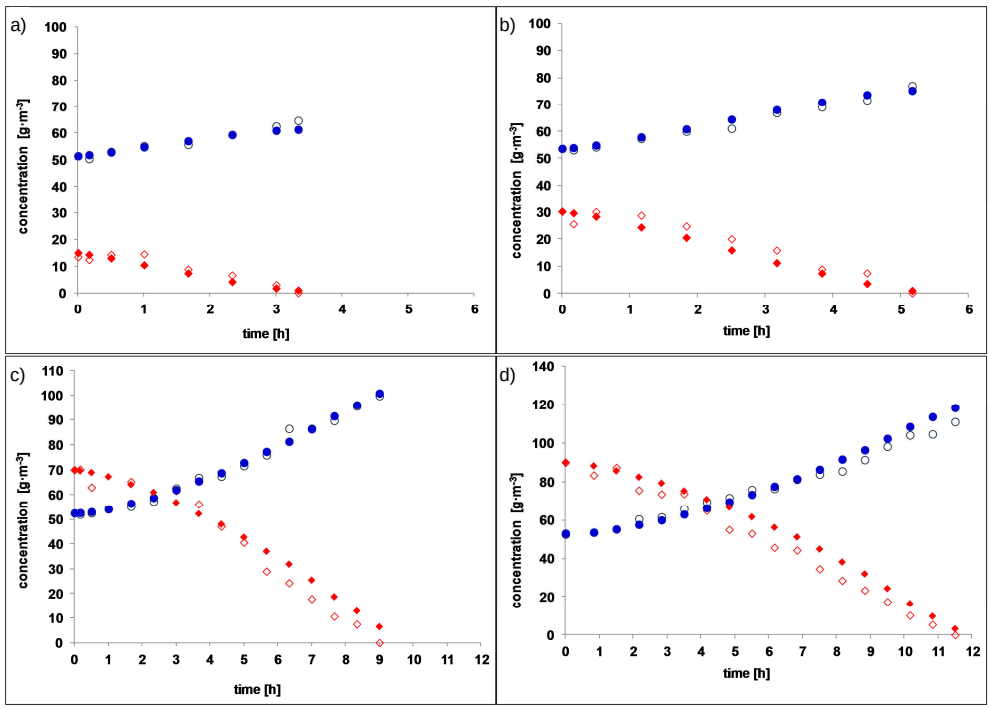

Fig. 3. Profiles of changes in concentration of biomass (circles) and styrene (diamonds) for different initial concentrations of growth substrate; *open symbols* - experimental values, *filled symbols* - values computed using set of eq. (3)-(4): a) S_l = 15 g·m^{-3}, b) S_l = 30 g·m^{-3}, c) S_l = 70 g·m^{-3}, d) S_l = 90g·m^{-3}

In Figure 3 the profiles of changes in biomass and styrene concentration calculated and obtained experimentally for a few periodic cultures of *Pseudomonas* sp. E-93486 cells were compared. It is worth emphasizing that the results of numerical simulations performed using set of eq. (3)-(4) fit the experimental values with good accuracy.

Purification of the air in pilot scale trickle-bed bioreactor (TBB)

The experiments of the air purification were performed in a pilot scale installation shown schematically in Figure 4.

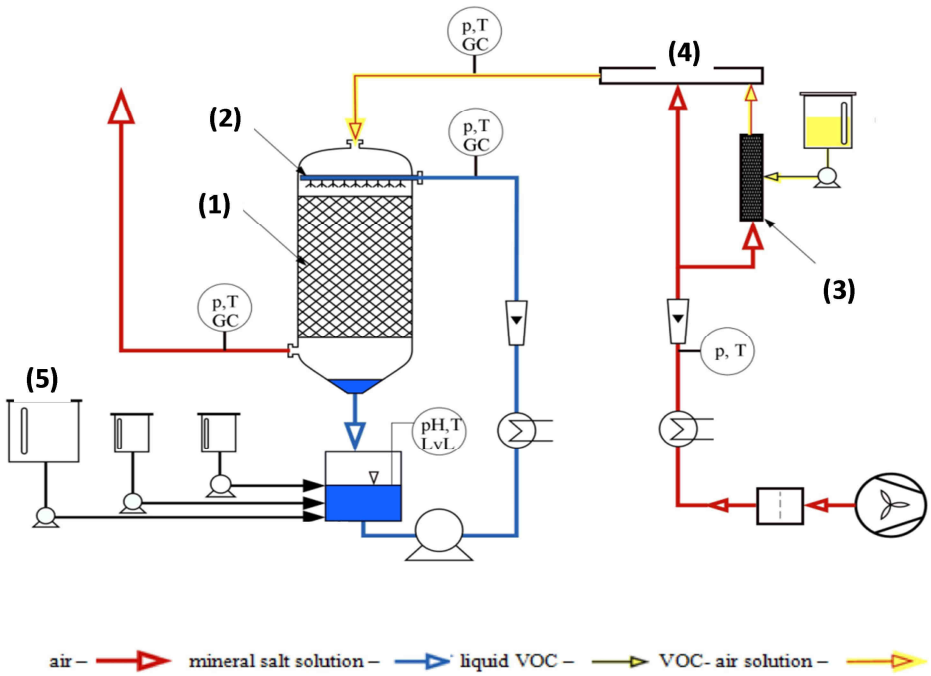

Fig. 4. Scheme of the experimental set-up: 1 - biofilter, 2 - sprinkler, 3 - vaporizer, 4 - mixer, 5 - reservoir of mineral salt solution

Its main part was a cylindrical column of 1.084 m I.D. filled with polypropylene Ralu rings up to the height of about 1.8 m. The air and liquid phases (mineral medium) flowed co-currently downward through the packing covered with a thick layer of the microorganisms. During experiments the concentration of styrene both on the inlet and the outlet of bioreactor was controlled in the gas and liquid phases. The detailed qualitative and quantitative analysis of microorganisms in the recirculating mineral solution was also performed every day. The effect of inlet styrene concentration on its degradation was studied for initial concentration in the air changing in the range of 0.2-1 $g \cdot m^{-3}$. The gas flow rate was changed in the range of 50-150 $m^3 \cdot h^{-1}$ whereas the liquid flow rate was maintained at the level 8 $m^3 \cdot h^{-1}$. The experiments were performed during the period of more than six months (Fig. 5).

It must be emphasized that conducted experiments showed high activity of examined bacterial strain in the styrene biodegradation; the conversion degree obtained for tested operational parameters changed in the range of 75-95%. It means that for the tested range of changes of pollutant load the high elimination capacity of the process was achieved; for

maximum pollutant load (80 $g \cdot m^{-3} \cdot h^{-1}$) about 2500 g styrene was removed from the air every day.

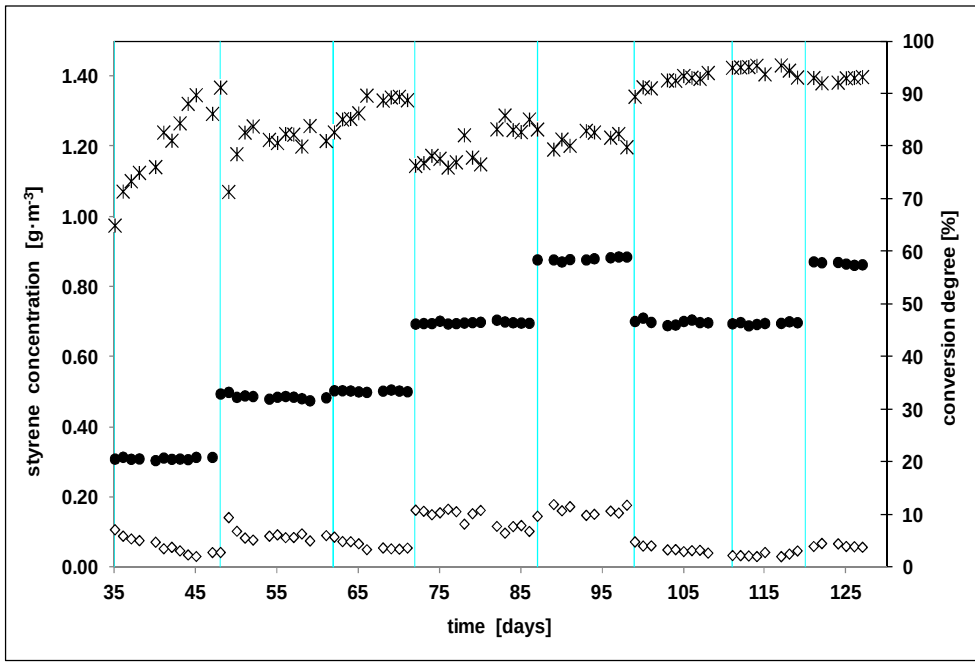

Fig. 5. Changes in the concentration of styrene in the air at the inlet (black circles) and outlet (white diamonds) of the reactor as well as conversion degree of the substrate (stars) during operation of the plant

Conclusions

The paper presents the issues associated with making use of microorganisms to remove the selected volatile organic compound which was the only source of carbon and energy for the examined strain. As a result of the kinetic experiments the equation describing the rate of the biological reaction of styrene oxidation by *Pseudomonas* sp. E-93486 bacteria were determined. The developed kinetic model was verified basing on our own experimental data base. It should be emphasized that the rate of biodegradation of the growth substrate is one of the most important stages of the processes taking place in bioreactor. The formulated relationships are necessary to verify the mathematical model of the bioreactor since drawing up mass balance of the compound removed from the air or sewage, regardless of the type of a bioreactor, always requires a knowledge of an expression determining the biodegradation rate of the removed pollutant. The tested strain was immobilized on the inert packing of TBB and for several months effectively decomposed styrene contaminating big stream of air. The created data-base will be used for verification of the mathematical model of the process of gas purification carried out in TBB.

The experiments showed high activity of tested microorganisms in the process of biodegradation of styrene and relatively low sensitivity to the inhibitory influence of

styrene at higher concentrations in solution (the high value of K_i). Due to such feature, the examined microorganisms may be recommended for technical applications as biological material in the processes of removing styrene from waste air and sewages.

References

[1] Bina B, Dehghanzadeh R, Pourmoghadas H, Kalantary A, Torkian A. Removal of styrene from waste gas stream using a biofilter. J Res Med Sci. 2004;6:280-288. http://www.jrms.mui.ac.ir/files/journals/1/articles/933/public/933-2601-2-PB.pdf.

[2] Djeribi R, Dezenclos T, Pauss A, Lebeault M-J. Removal of styrene from waste gas using a biological trickling filter. Eng Life Sci. 2005;5:450-457. DOI: 10.1002/elsc.200520092.

[3] The Clean Air Act Amendments of 1990 List of Hazardous Air Pollutants. www3.epa.gov/airtoxics/orig189.html.

[4] USEPA. https://www3.epa.gov/airtoxics/hlthef/styrene.html.

[5] Rueff J, Teixeira JP, Santos LS, Gaspar JF. Genetic effects and biotoxicity monitoring of occupational styrene exposure. Clin Chim Acta. 2009;399:8-23. DOI: 10.1016/j.cca.2008.09.012.

[6] Babaee R, Bonakdarpur B, Nasernejad B, Fallah N. Kinetics of styrene biodegradation in synthetic wastewaters using an industrial activated sludge. J Hazard Mater. 2010;184:111-117. DOI: 10.1016/j.jhazmat.2010.08.012.

[7] Ottengraf SPP, Diks RMM. Process technology of biotechniques. Dragt and van Ham. 1992;51:17-31. DOI: 10.1016/S0166-1116(08)70673-3.

[8] Iliuta I, Larachi F. Modeling simultaneous biological clogging and physical plugging in trickle-bed bioreactors for wastewater treatment. Chem Eng Sci. 2005;60:1477-1489. DOI: 10.1016/J.CES.2004.10.016.

[9] Arnold M, Rietta A, von Wright A, Martikainen PJ. Suihko M-LM. Bacterial degradation of styrene in waste gases using a peat filter. Appl Mocrobiol Biotechnol. 1997;48:738-744. DOI: 10.1007/s002530051126.

[10] Gąszczak A, Bartelmus G, Greń I. Kinetics of styrene biodegradation by Pseudomonas sp. E-93486. Appl Microbiol Biotechnol. 2012;93:565-573 DOI: 10.1007/s00253-011-3518-6.

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Abstrakt: Badano proces oczyszczania powietrza ze styrenu, substancji zaliczanej do grupy lotnych związków organicznych (LZO), prowadzony w pilotowym bioreaktorze strużkowym (TBB). Ponieważ najważniejszym etapem procesu oczyszczania powietrza z LZO w bioreaktorze strużkowym jest biologiczna reakcja jego rozkładu, zatem, projektując proces, należy przede wszystkim starannie wyselekcjonować mikroorganizmy efektywnie rozkładające usuwane z powietrza zanieczyszczenie, określić warunki najkorzystniejsze dla ich wzrostu oraz wyznaczyć kinetykę reakcji. W wyniku testów porównawczych wyselekcjonowano szczep efektywnie wykorzystujący styren jako jedyne źródło węgla i energii. Był to, pochodzący z kolekcji VTT (Finlandia), gram-ujemny szczep z rodzaju *Pseudomonas*, oznaczony symbolem E-93486. W testach wstępnych określono najkorzystniejsze dla jego wzrostu parametry (pH 7, 30ºC, DO = 5 mg·dm^{-3}) i zarówno eksperymenty kinetyczne, jak i proces oczyszczania powietrza w TBB prowadzono, utrzymując wyznaczone, optymalne dla reakcji biochemicznej warunki. Pierwszą serię eksperymentów kinetycznych przeprowadzono w reaktorze okresowym, zmieniając w kolejnych eksperymentach początkowe stężenie substratu wzrostowego w zakresie 5-90 g·m^{-3}. Badania wykazały inhibitujący szybkość wzrostu mikroorganizmów wpływ substratu, stąd do opisania kinetyki wzrostu E-93486 w obecności fenolu wybrano model Haldane. Zgromadzona baza danych doświadczalnych umożliwiła estymację stałych tego równania (μ_m = 0,119 h^{-1}; K_s = 5,984 g·m^{-3}, K_i = 156,6 g·m^{-3}). Hodowle ciągłe, prowadzone przy różnej szybkości rozcieńczania (D = 0,035-0,1 h^{-1}), umożliwiły określenie wartości współczynnika metabolizmu endogennego (m_d = 0,0165 h^{-1}) i maksymalnej wartości współczynnika wydajności biomasy ($(Y_{XS})_{max}$ = 0,913). Otrzymane pełne równanie kinetyczne wzrostu szczepu E-93486 w obecności styrenu zostało zweryfikowane przez porównanie obliczonych i otrzymanych eksperymentalnie profili zmian stężenia biomasy i styrenu. Badania procesu oczyszczania powietrza ze styrenu przeprowadzono w pilotowej instalacji,

której głównym elementem był bioreaktor strużkowy o średnicy 1,084 m, wypełniony na wysokość 1,84 m inertnym wypełnieniem (polipropylenowe pierścienie Ralu), na powierzchni którego unieruchomiony został testowany szczep. W badaniach strumień oczyszczanego gazu zmieniano w zakresie 50-150 $m^3 \cdot h^{-1}$, natomiast stężenie styrenu w powietrzu doprowadzanym do reaktora zmieniano w zakresie 0,2-1 $g \cdot m^{-3}$. Podczas trwających ponad 6 miesięcy eksperymentów uzyskano stopień konwersji styrenu rzędu 75-95%, co oznacza, że przy maksymalnym obciążeniu złoża (80 $g \cdot m^{-3} \cdot h^{-1}$) każdego dnia usuwane było z powietrza ~2500 g styrenu. Potwierdzona została w ten sposób skuteczność testowanej technologii oczyszczania powietrza z LZO.

Słowa kluczowe: styren, kinetyka, bioreaktor strużkowy