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# Purification processes –biodegradation of vinyl acetate from waste air in a trickle-bed bioreactor (TBB)

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The removal of vinyl acetate from waste gas in co-current gas-liquid downflow trickle – bed bioreactor inoculated with *Pseudomonas fluorescens* PCM 2123 strain was studied experimentally. Due to the lack of literature data, it was necessary to experimentally determine a rate of the partial stages of the process, which are: the rate of mass transfer process in the gas and liquid phases and the rate of biological reaction. The results of the experiments carried out in TBB were compared with the values obtained from mathematical model. The good compatibility of the calculated and experimental data was obtained.

## 1. Introduction

The most commonly applied methods of air purification from VOC are absorption, adsorption, cryocondensation and catalytic combustion. It is extremely difficult to purify the air polluted by low concentration of VOC and additionally with a large range of changes in VOC concentration. In this case biological methods of VOCs degradation turned out to be the most efficient. Their advantages are not only mild conditions of bioprocess (25-30 $^{o}$C, atmospheric pressure) but above all the fact that biodegradation does not shift the pollution problem to another environmental compartment (gas into solid or liquid) but decomposes it.

In the recent decades the attention was focused on variation of biofilters called trickle-bed bioreactor TBB. In this type of apparatus the packing of column is made up of inert material on which microorganisms are immobilized. The degraded pollution is the only source of carbon and energy for such microorganisms. Gas and liquid (mineral salt solution) phases flow co-currently down through the bed, which enables to clean large stream of gas with no fear of flooding the column. The research showed that TBBs are more effective than biofilters. Their advantages are both low investment and operational costs and larger potential of optimal operating parameters control (Alonso C., 1999).

The aim of the present work was to determine experimentally the efficiency of the biodegradation process of vinyl acetate contained in the air by means of *Pseudomonas fluorescens* PCM 2123 bacteria. Vinyl acetate is substrate for production of many polymers and copolymers, adhesives, acrylic finishes and emulsion paints. Over 4 million tons of vinyl acetate are used every year all over the world. So huge making use

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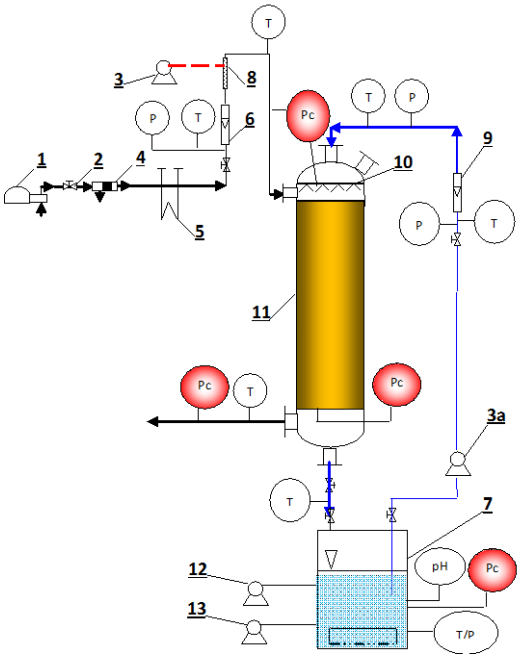
of this compound influences emission of its vapour to atmosphere. It is a harmful compound whose vapors irritate the mucous membranes of an eye and a respiratory system. Clinical research has confirmed its carcinogenic action inducing nose neoplasm.

## 2. Materials and methods

The research of the effectiveness of elimination of vinyl acetate from air was performed in a glass reactor having the inner diameter of 0.15 m (Figure 1).




1 – compressor, 2 – valve, 3 – pump dosing VOC, 3a – pump dosing reticulating mineral salt, 4 – air filter, 5 – heater, 6 – gas flow meter, 7 – container, 8 – evaporator, 9 – liquid flowmeter, 10 – sprinkler, 11- packed column, 12 – pump dosing KOH, 13 – pump dosing $KH_2PO_4$, T – temperature sensor, Pc – concentration measurement, P – pressure measurement, pH –pH measurement; , air - —, VOC - ----, mineral salt solution - -

*Figure 1: Schematic diagram of the experimental set-up.*

The air and liquid phases flowed co-currently downward through the column packed with polypropylene Ralu Rings (15x15 mm; ε = 0.94; a = 320 $m^2/m^3$) covered with a thick layer of the microorganisms (*Pseudomonas fluorescens* PCM 2123). The characteristics of bacteria, their adaptation to the VOCs and composition of recirculating mineral salt were presented in the earlier work (Greń et al., 2009). All experiments were carried out for steady – state and optimal, for the used microorganism, conditions (t= 303 K, pH=7, $pO_2$ = 7 $gm^{-3}$). During measurements the concentration of vinyl acetate both on the inlet and the outlet of bioreactor was

controlled in the gas phase. In the liquid phase the concentrations of degraded pollution and intermediate products of biodegradation (acetic acid, acetaldehyde, ethanol) were controlled in three points: on the inlet and the outlet of bioreactor and in the tank (7). These measurements were made by means of Chromatograph Varian Star 3800. The detailed qualitative analysis of microorganisms in the recirculating mineral solution was performed, among others, using Apilab NE20 test of Biomerieux firm, whereas quantitative analysis of bacteria was performed by means the spectrophotometric methods.

## 3. Experimental Results

In the processes of biopurification of air from VOCs, which are substances poorly soluble in water, the transport of pollution from gas phase through the liquid to biofilm surface is a very important stage. Unfortunately, it was noticed that the literature data concerning value of mass transfer coefficient for co-current downflow through the Ralu rings 15 mm of both phases (gas and liquid) was not available. The correlation describing the rate of biodegradation of vinyl acetate by bacteria *Pseudomonas fluorescens* PCM2123 was not available, either.

Therefore, before the beginning of the main process it was necessary to experimentally determine the rate of the partial stages of the process, which are: both the rate of mass transfer process in the gas and the liquid phases and the rate of biological reaction.

The rate of mass transfer in the liquid phase was determined using the process of the desorption of carbon dioxide from saturated with $CO_2$ water into air. For this system the resistance of mass transfer in the gas phase can be neglected because of high value of equilibrium constant. The results of experiments were correlated by means of an equation which was built –up with dimensionless modules of similarity:

$$Sh_z = 0{,}0156\,\mathrm{Re}_L^{0.342}\,Sc_L^{0.5} \tag{1}$$

In the gas phase it was determined by examining the absorption of ammonia from air into water. For this system mass transfer resistance occurs in both phases. Therefore, for determining of mass transfer resistance in liquid phase, the elaborated earlier equation (1) was used. The results of the experiments were correlated as the dependence:

$$Sh_g = 0.1527 \cdot \mathrm{Re}_g^{0.4073} \cdot \mathrm{Re}_L^{0.362} \cdot Sc_g^{0.33} \tag{2}$$

Both equations approximate the experimental data with an average absolute relative error $e_y \approx 2\%$. The following parameters, whose values were determined, where the specific growth rate of microorganisms and biomass yield coefficient. For that purpose the series of experiments were carried out in biostat for several initial concentrations of vinyl acetate. The culture medium was analyzed in order to determine the changes in time both of substrate and biomass concentrations. The collected data base enabled us to choose the form of a kinetic equation and to determine its constants. The following dependence was obtained:

$$\mu = \frac{0.1205 \cdot C_0}{C_0 + 17.41 + \dfrac{C_0{}^2}{168.35}} \tag{3}$$

The aim of the research carried out in TBB was to determine the range of changes of the biodegradation process parameters (such as gas and liquid flow rates, specific pollutant

load, oxygen concentration in the recirculating mineral salt solution), for which both high conversion degree K [%] of the biopurification process and lack of pollutant in the liquid phase were obtained. The recirculating mineral salt should contain neither vinyl acetate nor intermediate products of its degradation as e.g. acetaldehyde which is more toxic than the removed pollutant.
The results of biodegradation of vinyl acetate are plotted in Figure.2 as a dependence of a specific elimination capacity EC [$gm^{-3}h^{-1}$] vs specific pollutant load Ms [$gm^{-3}h^{-1}$].

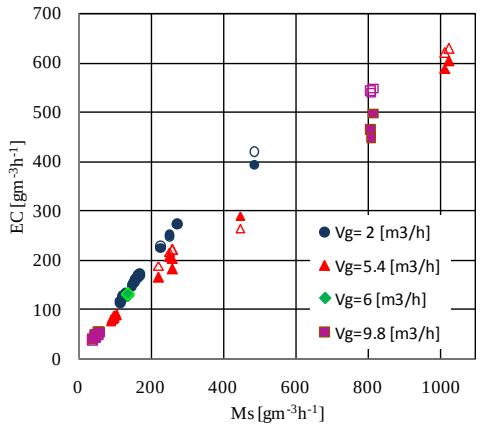



*Figure 2: Measured specific elimination capacity EC vs specific pollutant load Ms.Full points – experimental data; Empty points – calculated data (introduced below).*

It is worth emphasizing that every point in the plot represents an average value of, at least, one week measurement cycle. Measurements were carried out in two half-year series for the height of column bed H=0.45m and H=0.85 m and for volumetric gas flow rate changing from $V_g$= 2 to 9.8 $m^3h^{-1}$. No clogging of the column, due to excess growth of biomass on the packing material, was observed. The thickness of the biofilm can be indirectly controlled by the concentration of the pollutant and by the flow rate of the gas and liquid phases. The changes of biofilm thickness were signaled by increase of pressure drop in the column. After termination of measurements series the distribution of the microflora on the packing material was measured along the column in four points (column divided into four equal parts beginning from the top), and in cross section (for points – middle and rim).

## 5. Mathematical Description of Bioprocess

Based on the literature (Alonso, 1999; Diks, 1991; Hekmat, 1994; Mpanis, 1998) the mathematical description of biodegradation process in TBB was formulated. Biopurification process in TBB contains 4 stages: 1) mass transfer from bulk gas to the gas-liquid interface; 2) mass transfer from gas-liquid interface to the bulk liquid; 3) mass transfer from bulk liquid to liquid – solid interface; 4) simultaneous diffusion and reaction in biofilm.
Based on the simplifications described in literature mentioned above and assuming that the biological reaction is of first order (this assumption can be explain by poor solubility

substrate in water) dimensionless equations of mass balance for vinyl acetate in both phases are given.

In gas phase: $\frac{dY}{d\xi} + N_{og}(Y - Z) = 0$ (4)

In liquid phase: $\frac{dZ}{d\xi} - N_{og}E(Y - Z) + N_{R1}\eta_1 Z = 0$ (5)

with boundary condition-recirculation of the liquid:

$$\xi = 0 \quad Y = 1; \quad Z(0) = Z(1) \tag{6}$$

where: $\xi = \frac{z}{H}; \quad Y = \frac{C_g}{C_{g0}}; \quad Z = \frac{mC_L}{C_{g0}}$ (7)

In the above mentioned equations, the dimensionless parameters are defined as:

$$E = \frac{mw_g}{w_L}; \qquad N_{og} = \frac{k_{og}a_L H}{w_g}; \qquad N_{R1} = \frac{k_B a_v \delta_B H}{w_L} \tag{8}$$

The numerical procedure was worked out which enables to calculate the profile of the eliminated component in both phases (if all parameters of the model are known) or to estimate these parameters if the profiles of substrate concentration are known. Calculation were carried out on a PC in Turbo Pascal, using a forth – order Runge - Kutta procedure). The numerical procedure was tested using the data received by (Hekmat, 1994; Diks, 1991). The very good compatibility of the calculated and experimental data was obtained.

## 6. Conclusions

The carried out research enables us to create large experimental data base concerning biodegradation of vinyl acetate which let us determine the optimum parameters of the bioprocess.

The process proceeds optimally if it not only gains high efficiency of gas biopurification but also if there are neither substrate nor intermediate products in recirculating liquid. In the investigated process the appearance of acetic acid in the liquid phase is the first signal of bed insufficiency. That means that Krebs cycle is the lowest stage of vinyl acetate decomposition (Greń, 2009) what can be generally noticed for Ms>600. The conducted research confirmed the high efficiency of biopurification of air from vinyl acetate vapor. All parameters necessary for verification of the full process model were determined. There were mass transfer coefficients for both phases ($k_g$, $k_L$), specific growth rate of microorganisms and biomass yield coefficient (what enable us to calculate substrate utilization rate), density and thickness of biofilm layer.

## Nomenclature

$a_L$ - surface boundary area gas – liquid/liquid [$m^2\ m^{-3}$]

$a_V$ - surface boundary area gas – liquid/bioreactor volume [$m^2\ m^{-3}$]

$C_g$ - substrate concentration in core of gas phase [$g\ m^{-3}$]

$C_L$ - substrate concentration in core of liquid [$g\ m^{-3}$]

$d_e = 4\varepsilon/a$ – equivalent diameter of bed [m]

EC - specific elimination capacity [$gm^{-3}h^{-1}$]

K - conversion degree [%]
$k_B$ - constant rate processes in biofilm [$s^{-1}$]
$k_g$ - mass transfer coefficient in gas phase [m $s^{-1}$]
$k_L$ - mass transfer coefficient in liquid phase [m $s^{-1}$]
$k_{og}$ - overall mass transfer coefficient [$ms^{-1}$]
m - partition coefficient
Ms - specific pollutant load [$gm^{-3}h^{-1}$]
V - volumetric gas flow rate [$m^3s^{-1}$]
Y - dimensionless concentration in gas phase
Z - dimensionless concentration in liquid phase
$\beta'$ - mass transfer coefficient [kmol $m^{-2}$ $s^{-1}$]
$\delta'$ - dynamic diffusion coefficient [kmol $m^{-2}s^{-1}$]
$\delta_B$ - thickness of biofilm [ m]
$\zeta$ - dimensionless length of bed
$\eta_1$ - biofilm effectiveness factor
$\mu$ - specific growth rate [$h^{-1}$]

*Indices*
g - gas
H - length of column
L - liquid
o - inlet of reactor
x - axis x
z - axis z

*Dimensionless module*
$Re = w\gamma d_e/\eta$ - Reynolds number
$Sc = \eta/M\delta'$ - Schmidt number
$Sh = \beta' d_e/\delta'$ - Sherwood number
$Sh_z = \beta' \vartheta_Z/\delta'$ - modified Sherwood number

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