Clean processes – Biodegradation kinetics and mathematical modelling of microbial removal of vinyl acetate from dilute gaseous waste streams

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The aim of the present work was to determine experimentally the efficiency of the biodegradation process concerning vinyl acetate contained in the air, and to develop a mathematical model of this process. The fundamental and theoretical aspects of biological waste gas treatment in the trickling bioreactor was also presented. For a few months the process was carried out in the trickle-bed reactor, which was working at cocurrent downflow of both phases (the gas phase –air polluted with vinyl acetate, and the liquid phase – the solution of mineral salts). The reactor had been packed with polypropylene Ralu Rings (15x15 mm) forming a 0,7 m high layer and covered with a thin layer of biofilm (*Pseudomonas fluorescens* bacteria). The mathematical model of the process was formulated and verified using results of the experiments. In the mathematical model equations occur expression that describes kinetics of the biodegradation. In default of lack of literature data regarding this reaction, it was necessary to determine this expression experimentally. The experiments were carried out in the batch reactor (firm B.Braun) by measuring biomass growth and drop rates of vinyl acetate concentration as a function of time at the various initial vinyl acetate concentrations, at chosen temperature, pH, at constant aeration and composition of the mineral salt solution. The kinetics experiments were carried out for both "pure" Pseudomonas fluorescens strain and bacteria gained from the area of an industrial plant utilizing vinyl acetate (chemical firm Dwory – Oświęcim). The kinetics experiments were made in order to compare activity of the "pure" Pseudomonas fluorescens with a taken from the area of the industrial plant micro flora. The results of the experiments showed that vinyl acetate has inhibitory influence on biomass grow rate. Based on the experimental results the kinetic constants of equation describing bacteria grow rate were estimated. The empirical and theoretical aspects of biological waste gas treatment developed in this work will be the basis for proper design biodegradation process of vinyl acetate in the trickling bioreactor.

1. Introduction

1.1 Presentation of the state of affairs so far

Vinyl acetate (acetic acid ethenyl ester, $CH_3CO_2CH{:}CH_2$) is a representative of a wide group of compounds named Volatile Organic Compounds (VOCs). Among of

many air pollutants VOCs represent one of the most important groups of air pollutant. They are not only precursors for the formation of photochemical oxidants but also some species, like benzene, 1,3 butadiene and formaldehyde, are also known to be carcinogens (Clarke, A.G., Y.-H.Ko 1996,). Vinyl acetate is a extremely dangerous for environment and human life because of its properties and annual emission to the atmosphere. It is released to the environment, principally to the atmosphere, as a result of emissions from manufacturing, processing, and storage facilities. The industrial use of vinyl acetate is for the production of the polyvinyl acetate, polyvinyl alcohol and other polymers or copolymers. Its world wide annual production capacity was about 3 millions tons in 1982 and is still increasing (Nieder M., 1990). Populations living in areas surrounding hazardous waste sites may be exposed to vinyl acetate through inhalation of contaminated air and ingestion of or dermal contact with contaminated water. People who were exposed to vinyl acetate in air for short periods complained of irritation to their eyes , nose, and throat (Wiliam L., Roper M.D., 1992). The Environmental Protection Agency, (EPA) placed vinyl acetate on a list of 189 compounds the most onerous for environment. The biodegradation of VOCs in the Trickle Bed Bioreactors (TBR) can be used to abate the emission of volatile organic compounds from a wide range of industrial processes. Because of relatively low operating costs when compared with other abatement technologies, biodegradation of VOCs in the TBR often offers an economical solution, especially in cases where gas flows are high and component concentration are low. Additionally, biodegradation does not shift the pollution problem to another environmental compartment (gas into solid, solid into water etc.). Moreover, there is little secondary emission, which is not the case with incineration, adsorptive techniques, and chemical scrubbing (Disk R.M., S.P. Ottengraf, 1991)

1.2 Purpose of the work

The aim of the present work was to determine experimentally the efficiency of the biodegradation process concerning vinyl acetate contained in the air, and to present the fundamental and theoretical aspects of biological waste gas treatment in the trickling bioreactor. In the mathematical model describing process of biodegradation of vinyl acetate occurs expression that describes kinetics of the biodegradation. In default of lack of literature data regarding this reaction, it was necessary to determine this expression experimentally. The experiments were carried out in the batch reactor (firm B.Braun) by measuring biomass growth and drop rates of vinyl acetate concentration as a function of time at the various initial vinyl acetate concentrations, at chosen temperature, pH, at constant aeration and composition of the mineral salt solution. The kinetics experiments are still carried out for both “pure” Pseudomonas fluorescens strain and bacteria gained from the area of an industrial plant utilizing vinyl acetate (Chemical Firm Dwory – Oświęcim). The kinetics experiments are performing in order to compare activity of the “pure” Pseudomonas fluorescens with a taken from the area of the industrial plant micro flora. Based on the experimental results the kinetic constants of equation describing bacteria grow rate were estimated. The empirical and theoretical aspects of biological waste gas treatment developed in this work are the basis for proper design biodegradation process of vinyl acetate in the trickling bioreactor.

2. Materials and methods

The kinetics experiments were carried out by Pseudomonas fluorescens strain utilizing vinyl acetate. The experiments were made in the batch reactor – about volume 2 L (firm B.Braun) at the constant and optimal for *Pseudomonas fluorescens* conditions (temperature 30^{o}C, pH = 7 and aeration of the 4 to 7 mg · dm^{-3} of the dissolved oxygen in the solution). The reactor was filled up by solution of mineral salt and microorganisms which were "cleaned" and centrifuged before. The absorbance of the solution was about 0,18 in due to each experiment began at the same concentration of bacteria. The kinetic research of the vinyl acetate biodegradation were done for the various initial concentrations of the substrate, from S_0= 32 g · dm^{-3} to 400 g · dm^{-3}. The growth of the culture was followed by OD_{551} measurements in a spectrophotometer, the utilization of vinyl acetate and production of acetaldehyde and ethanol were measured by means of the gas chromatograph.

3. Results and discussion

The most often used relationship describing kinetics of biodegradation process is an Andrews equation presented below.

$$\mu = \frac{\mu_{\max} \cdot S}{(K_S + S)(1 + \frac{S}{K_i})} \tag{1}$$

where:

- K_s - half saturation constant, g·m^{-3}
- K_i, K - inhibition constant , g m^{-3}
- μ - specific growth rate, ·h^{-1}
- μ_{max} - maximum specific growth rate, ·h^{-1}
- S - substrate concentration, g·m^{-3}

In order to describe substrate biodegradation it was neccesary to estimate the relationship between the specific growth rate μ of the microorganisms and vinyl acetate concentration S. The key enzyme of the metabolic pathway was vinyl acetate esterase, which hydrolyzed the ester to acetate and vinyl alcohol. The latter isomerized spontaneously to acetalaldehyde which was dissproportionated into ethanol and acetate. The research of the biodegradation kinetics of vinyl acetate in the batch reactor include the series of experiments carried out for several initial substrate (vinyl acetate) concentration and at the same condition of process. The concentration range of vinyl acetate in the solution amount 32 gm^{-3} to 400 gm^{3}. The course of a single experiment for an initial concentration of vinyl acetate 500 ul (S_0= 310 gm^{-3}) was shown on a Fig.1. During microbial degradation of vinyl acetate are forming rough products acetic acid, acetaldehyde and trace amounts of the ethanol. The fluctuation of concentration of the substrate and rough products were made by help of chromatography analysis. Vinyl acetate undergoes also reaction of nonenzymatic hydrolysis forming acetate and vinyl alcohol, which is latter immediately transformed to its tautomeric form – acetaldehyde. In order to check influence of nonenzymatic hydrolysis on a biodegradation process of vinyl acetate was made experiment of degradation in the sterile medium (sterile mineral salt).

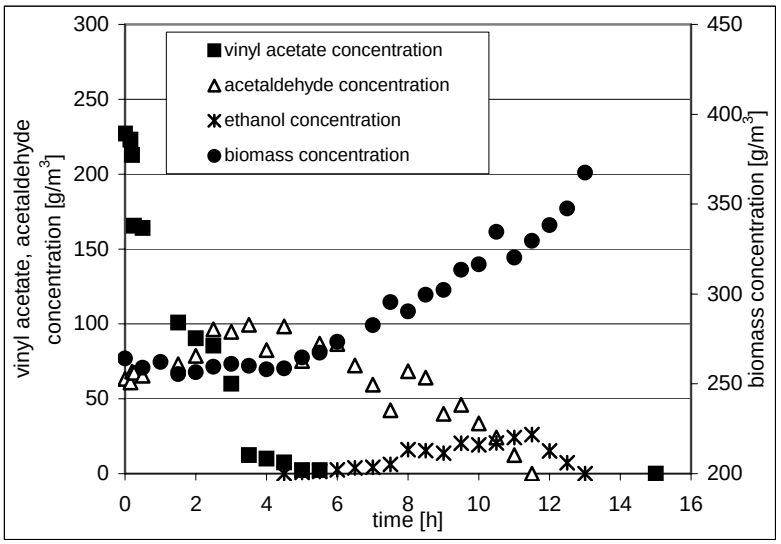

Fig.1. Variation of vinyl acetate, vinyl aldehyde and ethanol concentration as well as biomass concentration for aerobic biodegradation of vinyl acetate in a batch laboratory reactor (for $S_0 = 310\ g \cdot m^{-3}$)

The comparison of the vinyl acetate biodegradation and the abiotic hydrolysis of vinyl acetate for initial concentration S_0=186 gm^{-3} were presented in Fig.2. The total biodegradation of vinyl acetate for S_0=186 gm^{-3} was achieved after 2h, however nonenzymatic hydrolysis is about 3.2% at this same time.

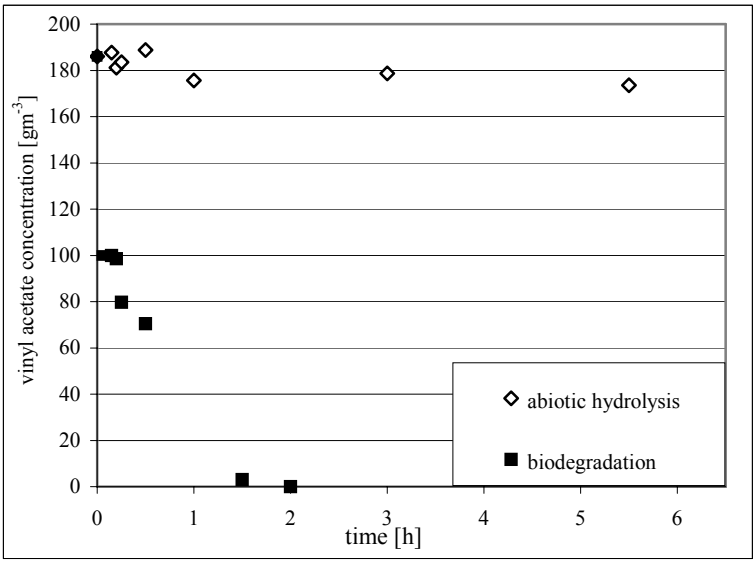

Fig.2. Comparison of vinyl acetate biodegradation time with its abiotic hydrolysis time (for $S_0 = 186\ g \cdot m^{-3}$)

Experimental data show that during growth of bacteria it is possible to determine the specific growth rate μ of the microorganisms which describe equation below (2). During the logarithmic growth of bacteria the specific growth rate μ is constant. The value of the specific growth rate μ can be estimate from the slope of linear semilogarithmic plot of biomass concentration versus time, during the exponential growth phase. It was presented in Fig.3.

$$\mu = \frac{1}{X}\frac{dX}{dt} \tag{2}$$

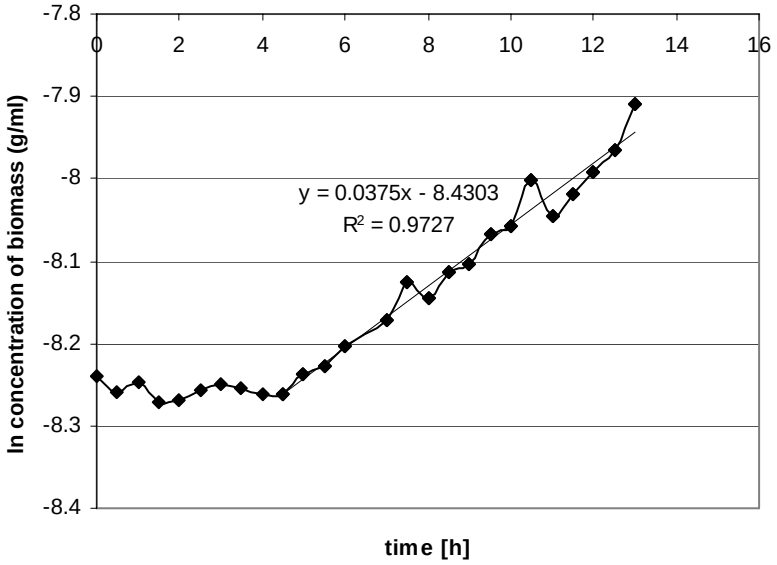

Fig.3. Estimation of specific growth rate from the semilogarithmic plot of biomass concentration versus time (for $S_0 = 310\ g \cdot m^{-3}$)

Bearing in mind equation (1) and taking an assumption that $K_i >> K_S$ the eqaution (1) has form:

$$\mu = \frac{\mu_{max} \cdot S}{K_S + S + \frac{S^2}{K_i}} \tag{3}$$

If the $K_i \rightarrow \infty$ the equation has a form of klasic Monods equation. The Edwards (Edwards V.H., 1970) offered two equations based on kinetics equations of enzymatic reactions:

$$\mu = \frac{\mu_{max} \cdot S \cdot (1 + \frac{S}{K})}{K_S + S + \frac{S^2}{K_i}} \tag{4}$$

$$\mu = \frac{\mu_{\max} \cdot S}{K_S + S + \frac{S^2}{K_i}(1 + \frac{S}{K})} \tag{5}$$

Estimation of parameters based on experimental data proved that equations (1), (3) and (5) give us a possibilities to achieve the results with an average (mean) percentage error lower than 11% what was presented in Fig. 4.

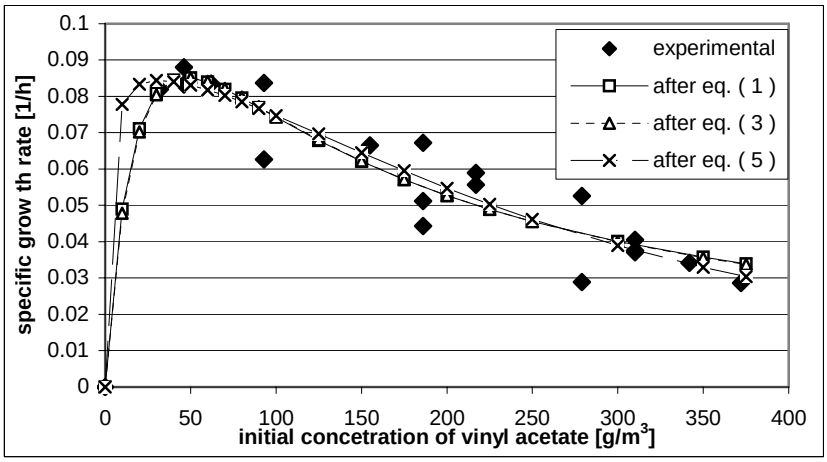

Fig.4. Effect of initial vinyl acetate concentration on specific growth rate.

The Edwards model, in the form presented in equation (5), was used to describe the dependence of the specific growth rate on the initial substrate concentrations. Based on the experimental results the kinetic constants (μ_{max} = 0,0935 [h^{-1}], K_s = 1,8887 [g · m^{-3}], K_i = 858,7 [g · m^{-3}], K=100,02 [g ·m^{-3}]) were estimated.

4. References

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