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Influence of Water Content on Degradation Rates for Ethanol in Biofiltration

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ABSTRACT

Treatment of ethanol vapor in a peat biofilter with various initial water contents (70%, 59%, 49%, and 35%) was studied. For water contents ranging from 49% to 70%, elimination capacity was about 30 g/m³/h. For a water content of 35%, elimination capacity decreased to 4 g/m³/h. A low mean CO_2 yield coefficient (0.35 g CO_2 produced per g ethanol consumed) was found for all of the initial water contents. The value was only 20% of the yield coefficient (1.91 g/g) predicted by stoichiometry. When the packing material was dried from 70% to 59% water content during the biofiltration process, elimination capacity dropped from 27 g/m³/h to 4 g/m³/h. After 24 hours of drying, the biofiltration experiment was restarted and run for two more weeks. During this period, the biofilter did not recover. At 59% water content, the rate of water evaporation was estimated at 59.6 g/m³/h. A simplified mass balance permitted calculation of the biological water production rate, approximately 22.1 g/m³/h.

INTRODUCTION

During the two last decades, biological processes (bioscrubbers, trickling beds, and biofilters) have been successfully employed to control volatile organic compounds (VOCs) and air toxics emitted from industrial facilities such as foundries, chemical plants, and print shops. They are competitive in applications involving treatment of large volumes of air containing low concentrations of pollutant. An advantage of biological processes is their low cost compared to other processes (incineration, absorption, adsorption, and condensation).

Biofilters are most commonly used to remove odoriferous compounds and VOCs. They are reactors packed with a wet material (e.g., compost, peat, or perlite) through which humid polluted air is passed. The packing material serves as a carrier for the microorganisms, nutrients, and water. The pollutant is transferred from the air to the biofilm, where it is biodegraded into carbon dioxide and water.

In the 1980s, development of biofiltration for control of VOCs and air toxics took place in West Germany and The Netherlands.[1] Currently, about 500 full-scale biofilters are running in these two countries. Recently, linked with stringent regulation of air emissions, biofiltration publications have appeared in other countries such as the United States,[2-3] Mexico,[4-5] Italy,[6] and France.[7]

Biofiltration has demonstrated the ability to eliminate alcohols,[2-9] toluene,[5] phenol,[6] ketones,[8] and petroleum fuel vapors.[10] To improve process design and performance, biofilter mathematical models have been developed. Steady-state approaches assuming zero or first order,[11-12] Michaelis-Menten,[5] and Haldane-type[2] degradation kinetics have been frequently used. More recently, a new approach taking into account single[3-13] or dual pollutants[8] described transient responses of biofilters. These studies and models allowed a better understanding of biofilter operation.

Biofilter operating conditions have received less attention. Temperature, pH, nutrient concentrations, water content, and air relative humidity are the most important parameters influencing biofilter elimination capacity.[1-14]

IMPLICATIONS

Efficient biofiltration of ethanol required support medium water contents above a minimum value. Severe drying caused irreversible damage to the medium and its microbial community. Biofilter operators must maintain water contents in the acceptable range, and strictly avoid the very dry conditions that may necessitate replacement of the medium.

In particular, water content is critical and must be controlled to avoid excessive wetting or drying of the filter bed. Heslinga[15] concluded that 75% of all problems with biofiltration are caused by poor humidity control. High moisture content may result in anaerobic zone development, high pressure drop, and washing out of microorganisms and nutrients. Low water content may reduce the sorption of gaseous pollutants or the survival and metabolism of the resident microorganisms. For most media, optimal water content ranges between 40 and 60% on a weight basis. Hodge[16] showed that water content has an important effect on the ethanol partition coefficient for compost and compost-diatomaceous earth filter material. A similar result was found by Martin et al.[17] for ammonia sorption on peat. Cox et al.[18] studied the influence of water content on the styrene elimination capacity of biofilters containing fungi on perlite, showing that a minimum water content (40%) was required to maintain maximum biological activity.

This paper describes the influence of water content on the elimination capacity for ethanol, which was selected for its rapid biodegradability. This work evaluates the minimum water content needed to maintain good elimination capacity in a biofilter. A simple mass balance allows calculation of water production.

MATERIALS AND METHODS

Experimental System and Packing Material

The biofilter was an 8-cm nylon column and with a 14-cm internal diameter (Figure 1). The packing material was contained in a chamber supported by a sieve plate. It was removable during the experiment, so the weight of the packing material could be determined. At the entrance of the biofilter, a bed of glass spheres provided homogeneous distribution of the inlet gas flow. Sampling ports were installed in the inlet and outlet tubing.

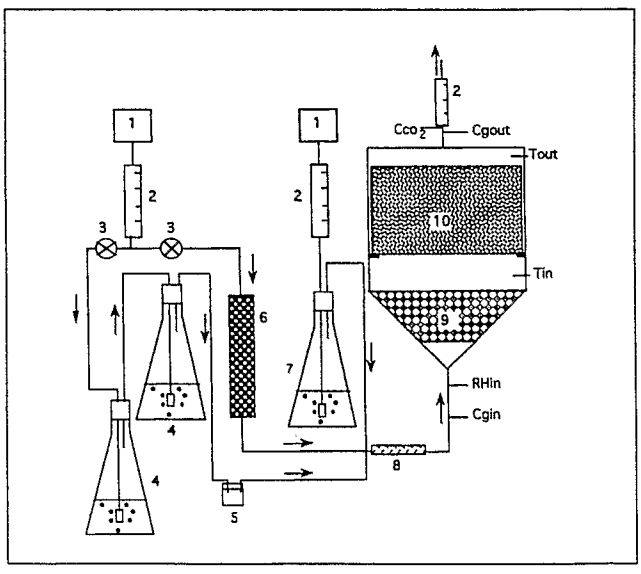

Figure 1. Schematic of the experimental biofilter showing: (1) air pumps, (2) air flow meters, (3) valves, (4) water, (5) cyclone, (6) silica gel, (7) ethanol, (8) static mixer, (9) spherical glass bed, and (10) removable basket.

Air was supplied by two peristatic pumps, and flow rates were measured with flow meters. One air stream passed through two 2-L bottles containing deionized water to provide humidification, while another was sparged into a 2-L bottle containing ethanol. The two streams were combined and the resulting main airstream flowed through a static mixer before entering the biofilter. A flow meter allowed the measurement of the total outlet air flow.

For drying experiments, air was passed through a silica gel column to obtain a relative humidity of 10% ± 6% before passing it through the biofilter.

The biofilter was filled with peat. At 0.04 $g/g_{\text{dry peat.}}$[5], $Ca(OH)_2$ was added as a pH buffer.

Inoculum and Medium Culture

The packing material was thoroughly inoculated with a mixed culture obtained from a biotrickling plant that treats VOCs. The culture medium composition was: K_2HPO_4, 0.8 g/L; KH_2PO_4, 0.2 g/L ; $CaSO_4 2H_2O$, 0.05 g/L ; $MgSO_4 7H_2O$, 0.5 g/L; $FeSO_4 7H_2O$, 0.01 g/L; and $(NH_4)_2SO_4$, 1 g/L. Inoculum, water, and mineral salts were added to the peat.

Analytical Methods

The concentrations of ethanol and CO_2 in the gas phase were measured by an SRI Model 8610 gas chromatograph equipped with a flame ionization detector. Data collection and integration was done by the SRI Peaksimple II program. Air was collected at the inlet and outlet of the biofilter using a 250 mL calibrated glass bottle. Three samples were taken in this bottle using a gas syringe (SGE) and 250 µL were injected into the gas chromatograph.

For determination of ethanol concentrations, a bypass column (10 cm long, 1 mm i.d.) with no packing was used, so that a peak was seen immediately after sample injection. The oven temperature was 120 °C. The carrier gas had a 10:1 ratio of air to hydrogen at flow rates ranging from 5 to 10 mL/min.

Table 1. Operating Conditions.

Inlet concentration	3.7 g/m³
Packing density	0.33 g/cm³
Air flow	25 L/h
Packed bed volume	1 L
Temperature	19 °C ±3 °C
Residence time (empty)	150 s
pH	7
Inlet air relative humidity	91% ±2%
Dry peat mass	300 g

Carbon dioxide concentrations were measured using a 60-m capillary column, 0.53 mm inner diameter, 5 μm df (Restek Corporation). To allow detection of CO_2 by flame ionization, a methanizer packed with nickel catalyst was attached in-line after the capillary column. With hydrogen used as the carrier gas, CO_2 was catalytically reduced to methane by passage through the methanizer. The methanizer was heated to 360 °C and the oven temperature was 30 °C. CO_2 concentration is defined as the difference between the measured concentration and the current mean atmospheric background concentration (350 ppmv).

The temperature of the air stream was measured by thermocouples at the inlet and outlet of the biofilter. A capacitance sensor (Humicap, Vaisala) was used to determine inlet air relative humidity. The weight of the packing material was obtained using a balance with a precision of ±0.1 g.

Operating conditions are described in Table 1.

RESULTS AND DISCUSSION

Elimination capacity (EC) was defined as the quantity of pollutant degraded per volume of filter material per time:

$$EC = (C_{gin} - C_{gout}) * Q/V \text{ (g/m}^3\text{/h)} \quad (1)$$

where C_{gin} = inlet gas concentration (g/m³), C_{gout} = outlet gas concentration (g/m³), Q = gas flow rate (m³/h), and V = volume of biofilter packing material (m³).

During steady state elimination of ethanol, water evaporation and production rates were included in a mass balance:

$$dM_t/dt = -dM_{ev}/dt + dM_{wp}/dt \text{ (g/m}^3\text{/h)} \quad (2)$$

where dM_t/dt = rate of change of the total mass (g/m³/h), dM_{ev}/dt = rate of water evaporation (g/m³/h), and dM_{wp}/dt = production of water (g/m³/h) .

Influence of the Initial Water Content

C_{gin} was maintained at approximately 3.7 g/m³ during the experiments (Figures 2-5). Small variations of RH_{in} (inlet relative humidity), T_{in} (inlet temperature), and T_{out} (outlet temperature) were observed for the four experiments (Table 2). RH_{in} and the difference between T_{in} and T_{out} were around 90% and 0.5 °C, respectively.

During start-up, ethanol adsorption on the wet peat seems to have been the predominant phenomenon. For the two lowest values of initial water content (W_i = 49%, 35%) less ethanol was adsorbed. This can be explained by the high solubility of ethanol in water and the low adsorption capacity of dry peat.[16] For all the experiments, steady state conditions were attained after six days of operation. Beyond this time, the microorganisms were active and degrading ethanol. The average differences between C_{gin} and C_{gout} were 1.1 g/m³, 1.3 g/m³, 0.94 g/m³, and 0.07 g/m³ for 70%, 59%, 49%, and 35% initial water content, respectively.

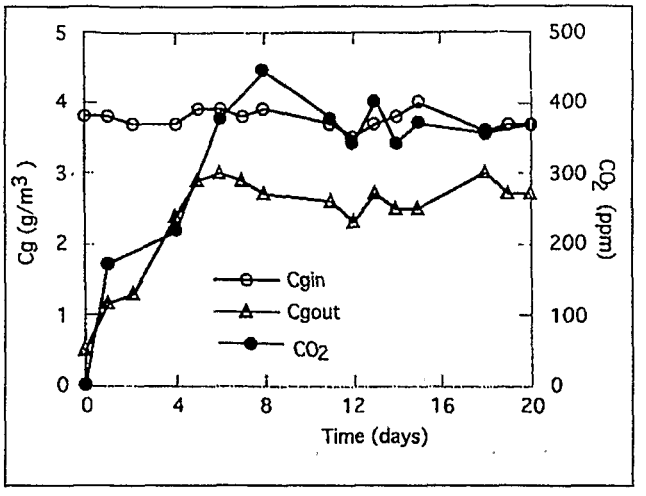

Figure 2. CO_2, inlet, and outlet ethanol concentrations with time for an initial water content of 70%.

At the beginning of each experiment, a peak of CO_2 release was observed. Although the data are not sufficient for a certain explanation, it is possible that acidification from organic acid production caused the CO_2 release by conversion of existing carbonate in the peat.[16] At steady state, the average CO_2 concentrations were 366 ppmv, 133 ppmv, 142 ppmv, and 32 ppmv (above ambient atmospheric concentrations) for 70%, 59%, 49%, and 35% initial water content, respectively. For the highest W_i of 70%, the exceptionally high CO_2 release may have been due to more oxidation of the ethanol to CO_2, instead of production of organic acid intermediates. The final pH for this experiment was 6.2, above the average of 5.3. Devinny and Hodge[19] have shown that ethanol consumption was associated with production of acetaldehyde, acetic acid, and ethyl acetate. For the experiment with a W_i of 35%, low CO_2 production is attributable to the very low ethanol degradation rate.

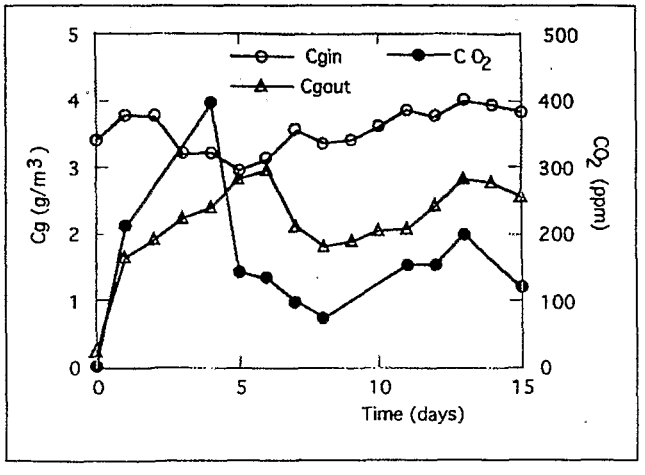

Figure 3. CO_2, inlet, and outlet ethanol concentrations with time for an initial water content of 59%.

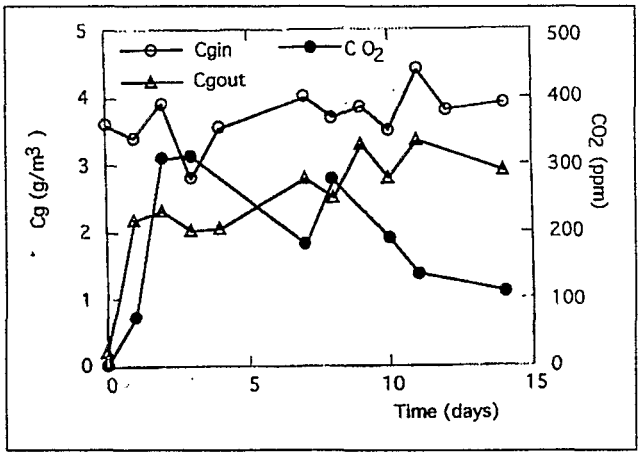

Figure 4. CO_2, inlet, and outlet ethanol concentrations with time for an initial water content of 49%.

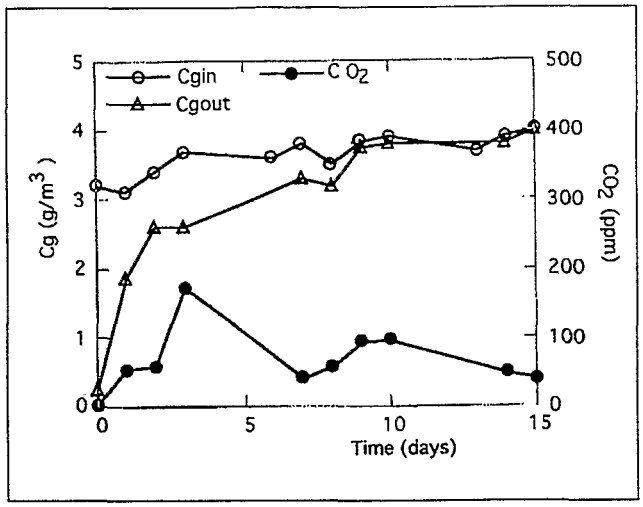

Figure 5. CO_2, inlet, and outlet ethanol concentrations with time for an initial water content of 35%.

The mean experimental CO_2 yield coefficient (g CO_2 produced per g ethanol consumed) for the three experiments (W_i = 70%, 59%, 49%) was 0.35 g/g. This value is low compared with the theoretical yield coefficient (1.91 g/g) obtained using the stoichiometry of complete oxidation.[16] This difference may result from diversion of carbon to production of secondary products and biomass.

The elimination capacity (EC) decreased substantially when W_i was less than 49% (Figure 6). For initial water contents ranging from 59% to 70%, EC was about 30 g/m³/h. For W_i=35%, EC was only 4 g/m³/h. First, the partition coefficient, k_h (pollutant concentration in the solids-water phase divided by the pollutant concentration in the air phase) varies strongly with water content. Hodge and Devinny[9] showed that water content had a major effect on the ethanol k_h values for the compost and compost/diatomaceous earth filter material, suggesting that the dry materials had poor capacity to absorb the ethanol in comparison to the wet materials. Second, reducing the water content of the peat from 49% to 35% reduced the water activity of the peat from 1 to 0.98. This value might be insufficient for high biological activity.[20] A similar result was obtained by Cox et al.,[18] who studied the influence of water content on the styrene elimination capacity of biofilters containing fungi on perlite. They observed a 50% decrease of EC when the water activity dropped from 1.0 to 0.98, corresponding to 60% and 30% water content, respectively.

Table 2. Inlet, outlet temperatures and inlet air relative humidity for different initial water contents. T_{in}, T_{out}, and RH_{in} are the average values obtained during each experiment.

W_i(%)	T_{in}(C) ±2 °C	T_{out}(C) ±2 °C	RH_{in}(%) ±2%
70	18.2	18.6	90.5
59	20.6	21.1	89
49	19.9	20.6	91.5
35	20.1	20.6	91

Studies in microcosms showed that a 30% reduction in headspace toluene consumption was obtained with water contents below 50% in samples from a biofilter.[21]

Drying during Biofiltration

The drying experiment was begun with an initial water content of 70% (Figure 7). After six days, the biofilter reached steady state, in terms of treatment efficiency, and the average elimination capacity was about 27 g/m³/h. On the twentieth day, the peat was dried over 24 hours using an inlet air relative humidity of 10% ± 6% and air flow of 250 L/h. The air temperature was not increased and was close to the ambient air temperature (19 °C ± 2 °C). The inlet ethanol concentration was maintained at 4 g/m³ ± 1 g/m³. After drying, the initial air relative humidity of 91% was restored. Two days were needed to reach a new steady state.

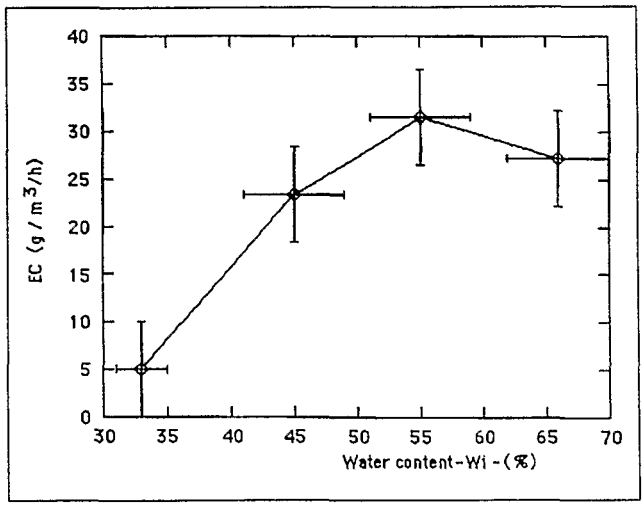

Figure 6. Elimination capacity of ethanol for different initial water contents of the peat. Vertical bars represent the standard errors. Horizontal bars represent the range of the water content for each experiment.

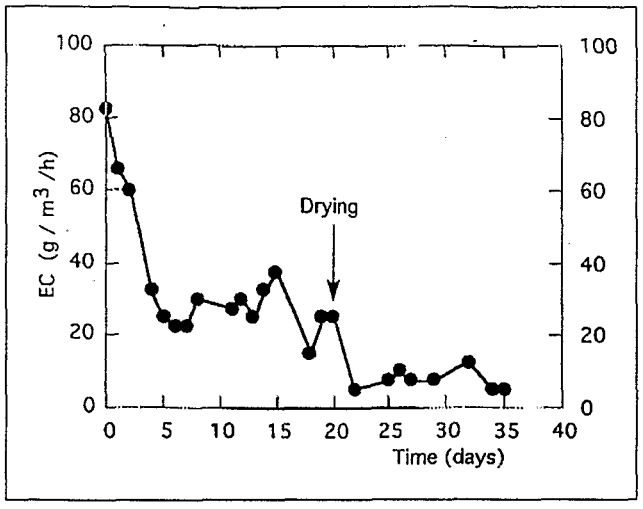

Figure 7. Elimination capacity for ethanol over time. The arrow designates the time at which the biofilter was dried.

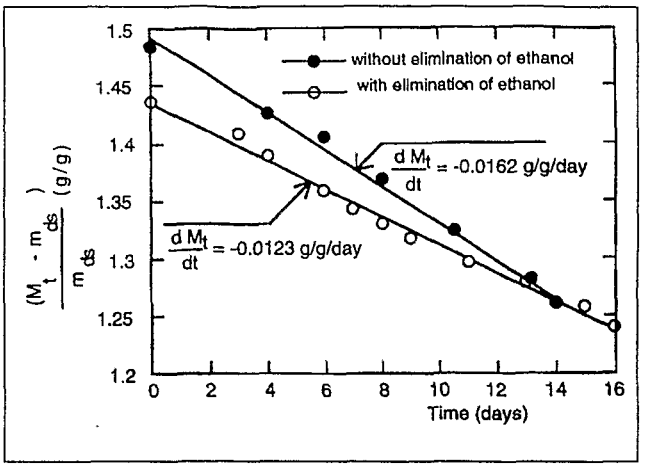

Figure 8. Total weight variation of peat with time. (o) represents biofiltration for 59% initial water content. (•) represents biofiltration after drying of the peat. The weight of dry support is m_{ds}.

During 24 hours of drying, the water content decreased from 70% to 59%. The subsequent mean value of EC (4 g/m³/h) was very low compared with the ECs measured for biofilters with initial water contents in this range (Figure 6). Water content should not have been a limiting parameter for the bacterial growth. The *decline* in water content, rather than its final value, seems to have been the damaging factor.

The most active microorganisms degrading the ethanol were located in the outer layers of the biofilm. The direct contact between the biofilm and dry air stream might have played a role in the inactivation or death of the ethanol-degrading microorganisms.

The decrease of EC might also result from porosity changes in the medium. Support matrix compaction might induce the development of lumps through which the polluted air does not flow. In this case, the effective biolayer surface area decreases, and flow is channeled. However, the change in bed porosity with water evaporation was small (7%) under the conditions studied. No compaction of the packing was noted during or after the drying period. Tracer experiments were done before and after the drying, and no difference in the smoke flow distribution was observed at the outlet of biofilter. In both cases, flow was homogeneous, and no channeling effects were detected. For hydrophilic compounds like ethanol, a decrease of water content might reduce the value of the ethanol partition coefficient. However, results obtained in this paper showed that initial water contents in the range from 70% to 59% do not modify biofilter performance. The EC was about 27 g/m³/h for a range of the water contents from 50% to 65% (Figure 6), corresponding to 1.0 g water/g dry peat and 1.85 g water/g dry peat, respectively.

Mass Balance

The biofilter used in the drying experiment ultimately showed extremely low biological activity. This allowed an evaluation of the effect of biologically produced water on the overall water mass balance. During all of the experiments, the weight of the peat was measured. The variation of weight with time was plotted for an initial water content of 59% (the experiment shown in Figure 3), where the rate of change of total mass, dM_t/dt, was -0.0123 g/g/day or -37.5 g/m³/hr. For the period after drying (Figure 8), which also began with a water content of about 59%, ethanol biodegradation was negligible (EC = 4 g/m³/hr). It can be assumed that the biomass and biological water production were also negligible. Here, where the inlet air humidity was about 90%, dM_{ev}/dt was equal to $-dM_t/dt$ (eq 2). The amount of water vapor was 0.0162 g/g/day or 56.6 g/m³/hr.

The operating conditions for an initial water content of 59% are reported in Table 2. For the drying experiment, T_{in}, T_{out}, and RH_{in} were 20.3 °C, 20.8 °C, and 90.3%, respectively. It was assumed that the output air was saturated with water vapor (RH_{out} = 100%). In addition to the column weighing procedure, for each of these two experiments, dM_{ev}/dt was calculated using the input and output vapor partial pressure, and equaled dM_{ev}/dt were 62.6 g/m³/hr and 59.6 g/m³/hr. A small difference was found between determinations for the two methods. Figure 8 shows that the water loss was slower in the active biofilter because of biological water production; the water production can be estimated at 59.6 g/m³/hr - 37.5 g/m³/hr = 22.1 g/m³/hr. The water production was estimated at 36 g/m³/hr when it was assumed that all of the ethanol removed in the active biofilter was converted to water. The discrepency likely occurs because some ethanol is converted to secondary metabolites and biomass.

CONCLUSIONS

The influence of the water content on the elimination capacity of ethanol in biofiltration with peat was shown. Below a water content of 49%, EC dropped from 27 g/m³/h to

4 g/m³/h. For a water content of 59% and the operating conditions of this experiment, the rates of water evaporation and biological water production were 59.6 g/m³/h and 22.1 g/m³/h, respectively. When the packing material was rapidly dried, the biofilter lost most of its treatment capacity, even though the final water content was not very low. Performance did not recover within two weeks.

During the drying of the biofilter, numerous phenomena can occur simultaneously. Change in the water content modifies the partition coefficient, bed porosity, hydrodynamic air flow, biomass activity, etc. Study of isolated factors is difficult. To study the influence of different parameters on biofiltration, other supports, such as porous ceramic and granular actived carbon, might be used. The use of these supports avoids changes in bed porosity and hydrodynamic air flow during drying. Biomass estimation could be easier with an inorganic medium.

The conclusion that the effects of drying were not readily reversible has consequences for practical applications. Biofilters that are inadvertently allowed to dry rapidly, even if the final water content is in the normal range, may require replacement of the support medium, rather than simple rewetting. This is an expensive process and must be avoided through the use of procedures for monitoring and automatic shutdown if the watering system fails.

LIST OF ABBREVIATIONS

C_{gin} = inlet gas concentration (g/m³)
C_{gout} = outlet gas concentration (g/m³)
EC = elimination capacity (g/m³/h)
M_t = mass of total support (g)
M_{ev} = mass of evaporated water (g)
M_{wp} = mass of produced water (g)
Q = gas flow rate (m³/h)
Rh_{in} = inlet air relative humidity (%)
Rh_{out} = outlet air relative humidity (%)
T_{in} = inlet air temperature (°C)
T_{out} = outlet air temperature (°C)
V = volume of biofilter packing material (m³)
W_i = initial water content of the biofilter bed (w/w)

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