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Pervaporation-biological oxidation hybrid process for removal of volatile organic compounds from wastewaters

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Abstract

A new pervaporation-biological oxidation hybrid process for the treatment of wastewaters containing volatile organic compounds (VOCs) has been investigated. The process combines pervaporation using a sweep gas with absorption and biological degradation of the permeate VOCs. A model system with monochlorobenzene (MCB) as the VOC and *Pseudomonas* JS150 as the degrading microorganism was used for the study. Relatively high temperatures for the pervaporation operation were used, allowing the use of lower membrane area and lower sweep gas flowrate. The resulting higher concentration of VOC in the sweep gas and the difference in temperatures between pervaporation unit and bioreactor, were expected to improve the mass transfer of VOC from the gas into the biomedium, leading to a better VOC removal from the gas stream. The performance of this system, working at a constant gas flowrate and a bioreactor temperature of 30°C, was studied for step increases in pervaporation temperature. Raising the temperature was shown to increase the mass transfer flux in the membrane module. Bioreactor removal efficiencies close to 100% were obtained throughout, and an elimination capacity of 84 g (MCB) m^{-3} h^{-1} was attained. The system was then run with a lower bioreactor temperature (15°C), in order to accurately quantify changes in removal efficiency with varying pervaporation temperature. In this case, a constant VOC load was fed to the bioreactor, with reductions in gas flowrates concomitant with increasing pervaporation temperatures. It was shown that using lower gas flowrates with higher VOC concentrations, at higher temperatures, resulted in significantly improved removal efficiencies. Concentrations of 17 g m^{-3} of MCB [1] were treated in the bioreactor working at 15°C, with removals of 95%.

Keywords: Pervaporation; Biodegradation; Volatile organic compounds; Hybrid process; Monochlorobenzene

1. Introduction

Volatile organic compounds (VOCs) are present in effluents from industries such as petroleum refineries and chemical plants. Many of these compounds are considered priority pollutants by the US Environmental Protection Agency. Their negative effects on health and environment include depletion of stratospheric ozone, ground level smog formation, odours and chronic toxicity [1]. The global warming potential of chlorinated hydrocarbons is considered to be many times that of carbon dioxide [2]. In addition, a significant number of these compounds are carcinogenic. There is clearly a need to prevent the discharge of these compounds into the environment.

The treatment of waste streams containing VOCs using membrane technologies has been widely researched. Membrane separation technologies offer advantages over conventional mass transfer processes, such as high selectivity, compact and modular design

[1] Throughout the text, gas concentrations and gas flowrates are at standard temperature and pressure, STP (temperature = 0°C, pressure = 1 atm).

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Nomenclature

A	membrane area (m^2)
$C_{g,i}$	molar concentration of i in the gas phase ($mol\,m^{-3}$)
$C_{l,i}$	molar concentration of i in the liquid phase ($mol\,m^{-3}$)
F_g	gas flowrate ($m^3\,s^{-1}$)
F_l	liquid flowrate ($m^3\,s^{-1}$)
J	flux through the membrane ($mol\,s^{-1}$)
k_l	liquid mass transfer coefficient in terms of concentration driving force ($m\,s^{-1}$)
$k_l a$	volumetric liquid mass transfer coefficient (s^{-1})
$K_{ov,l}$	overall mass transfer coefficient in terms of liquid concentration driving force ($m\,s^{-1}$)
P	total pressure (Pa)
P^0	saturation vapour pressure (Pa)
p_g	gas partial vapour pressure (Pa)
p_l	liquid partial vapour pressure (Pa)
P_{mem}	intrinsic permeability through the membrane ($mol\,m\,m^{-2}\,Pa^{-1}\,s^{-1}$)
Q_l	liquid mass transfer coefficient in terms of partial vapour pressure driving force ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$)
Q_{mem}	membrane mass transfer coefficient in terms of partial vapour pressure driving force ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$)
Q_{ov}	overall mass transfer coefficient in terms of a partial vapour pressure driving force ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
Re	Reynolds number
r_{in}	inner radius (m)
r_{ou}	outer radius (m)
Sc	Schmidt number
Sh	Sherwood number
T	temperature (K)

Greek letters

γ	activity coefficient
γ^∞	infinite dilution activity coefficient
ρ_g	gas molar density ($mol\,m^{-3}$)
ρ_l	liquid molar density ($mol\,m^{-3}$)

[3], potential for independent variation of gas and liquid flowrates without problems such as flooding, loading or weeping, and high volumetric mass transfer coefficients [4]. Pervaporation [5–7] and vapour permeation [8,9] have been applied to wastewaters and waste gases containing VOCs, removing the VOCs from the contaminated streams and allowing their recovery [10,11] or elimination [12]. Other membrane processes have been applied to waste streams containing VOCs, combining absorption and stripping [4], pervaporation through liquid membranes [11] or membrane separation followed by biodegradation of the organic compounds [13,14].

Pervaporation consists of selective transport through a non-porous polymeric membrane combined with a phase change from liquid to vapour [15]. A vacuum is usually applied to the permeate side to effect vaporisation of the organic solutes, but a sweep gas may be used as an alternative means of lowering the partial pressure [15,16]. The organic solutes, along with some water, dissolve in and diffuse through the membrane, are collected on the permeate side, and are subsequently condensed [11]. High vacuum is costly [7], although vacuum pervaporation seems to give higher fluxes than sweep gas pervaporation [10]. For sweep gas pervaporation, the condensation costs are likely to be higher due to additional resistance to heat transfer and additional cooling load presented by the noncondensable gas, increasing the heat-exchanger area required (capital costs), and the energy load (operating costs).

After condensation, the permeate may be separated into two phases, and the organic compound(s) recovered and reused. In order to be efficient and economically advantageous, recovery processes usually require highly concentrated waste streams and a high value of the compounds to be recovered. Additionally, mixtures of organic compounds might result in a condensate with no suitable use [17]. Pervaporation alone is unable to provide (at least economically) both a high purity retentate and a high purity permeate [3], and where recovery is not reasonably possible, a destruction process such as thermal, catalytic or biological oxidation follows.

In this work, a new pervaporation-biodegradation hybrid process is investigated, which combines pervaporation using a sweep gas with the biological treatment of the permeate VOCs in the sweep gas. Rather

than utilising condensers, a reaction is employed to consume the VOC after its absorption into a liquid phase. Due to the attractiveness of biological methods in terms of low cost and operational simplicity [18], and since many toxic VOCs can be biologically degraded using suitable aerobic microorganisms [19], a biodegradation reaction was chosen to eliminate the VOCs. The driving force for transfer of the pollutants from the gas into the liquid phase is maintained by the biological mineralisation of the pollutants in the liquid.

A relatively high temperature for the pervaporation operation is coupled with a lower temperature for the biodegradation. Increasing the temperature in the membrane module will favour the transfer of a VOC from a liquid into a gas phase, as volatility is strongly dependent on temperature. This leads to a much lower membrane area requirement for the same VOC removal from the wastewater. It also allows the use of a lower sweep gas flowrate for the same removal, as an increase in temperature increases the saturation concentration of VOCs in the stripping gas.

The sweep gas flowrate to the bioreactor is relatively low, is concentrated in VOCs, and is above the bioreactor operating temperature. Both the high VOC concentration and the lower temperature in the bioreactor favour VOC transfer from the gas into the liquid, where biodegradation occurs. For the case of poorly water soluble compounds, where mass transfer into the liquid phase is the limiting step, this process is expected to improve the overall efficiency.

2. Experimental procedure

Monochlorobenzene was used for all experiments as a model volatile organic compound, as it is a typical VOC, it is not easily biodegradable [20], and the release of chloride ion may be used as a confirmation of removal of MCB by biodegradation [13].

A schematic of the pervaporation-bioreactor system is shown in Fig. 1. The membrane module consisted of a single 0.62 m long section of silicone rubber (70% polydimethylsiloxane (PDMS) + 30% silica filler) tubing, (3.0 mm i.d. with 1 mm wall thickness; Esco Rubber, UK), mounted concentrically in a glass shell. Inside the membrane, a synthetic wastewater containing MCB was recirculated at a constant flowrate. A continuous feed of an aqueous MCB solution with a concentration of approximately $400\,g\,m^{-3}$ was supplied to the recirculating solution reservoir, and an equal flow was withdrawn from it. Outside the

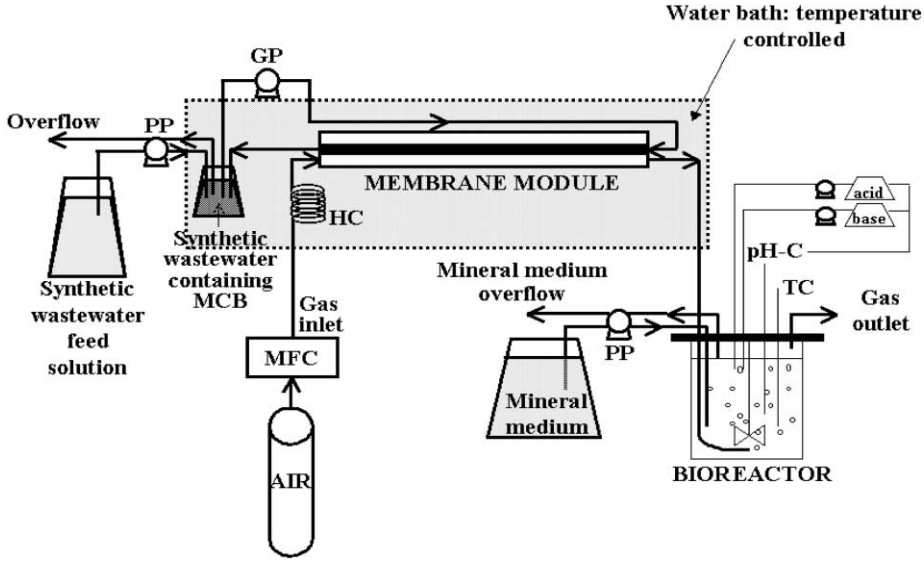


Fig. 1. Experimental pervaporation-bioreactor hybrid process for removal of volatile organic compounds from wastewater. PP: peristaltic pump; GP: gear pump; MFC: mass flow controller, HC: heating coil, pH-C: pH controller, TC: temperature controller.

membrane tube, air was passed in a counter-current direction to the recirculating solution to air-strip the MCB that crossed the membrane. The air stream flowrate was controlled by a mass flow controller (Tylan, UK). The flowrates were varied between 0.05 and 0.40 $dm^3\,min^{-1}$.

The membrane module, the recirculating MCB solution reservoir, and a metal coil to pre-heat the air prior to its entering in the membrane module, were immersed in a temperature controlled water bath. Four temperatures were studied: 30, 50, 60 and 70°C. The temperature was monitored using thermocouples in the recirculating MCB solution, at the air inlet and outlet, respectively, of the membrane module, and in the bioreactor. It took 3–4 h for the temperature in the system to reach the setpoint value after it had been changed. MCB concentration was measured in the feed solution, in the recirculating solution, and at the air outlet of the membrane module.

The air outlet from the membrane module was scrubbed in the bioreactor. The bioreactor was operated as a continuous stirred tank bioreactor, with a working volume of 2 l (SGE, France), filled with 1.5 l of mineral medium, unless otherwise stated. It was equipped with a pH controller to maintain the pH at 7.00 ± 0.10, with a temperature controller, and stirred at 820 rpm by a Rushton turbine. Fresh mineral medium was added continuously using a peristaltic pump, with an equal flow being withdrawn from the bioreactor, leading to a dilution rate of $0.09\,h^{-1}$. The composition of the mineral medium is given in Table 1. The bioreactor was inoculated with a culture of *Pseudomonas* sp. strain JS150, capable of utilising MCB as a sole source of carbon and energy. This culture was kindly supplied by Dr. S. Nishino of USA Air Force Tyndal Base, FL (USA). MCB concentration was measured at the gas outlet of the bioreactor and in the biomedium. MCB degradation was monitored by its disappearance from the gas stream and confirmed by the release of chloride ion in the biomedium.

Table 1
Mineral medium composition

Compound	Concentration ($mg\,dm^{-3}$)
KH_2PO_4	1326
Na_2HPO_4	866
$(NH_4)_2SO_4$	1000
$MgSO_4{\cdot}7H_2O$	200
Trace elements	
$CaCl_2$	2.65
$FeSO_4{\cdot}7H_2O$	1
$ZnSO_4{\cdot}7H_2O$	0.05
H_3BO_3	0.05
$CoCl_2{\cdot}6H_2O$	0.05
$MnSO_4{\cdot}5H_2O$	0.02
$Na_2MoO_4{\cdot}2H_2O$	0.015
$NiCl_2{\cdot}6H_2O$	0.01

In the first set of experiments, the bioreactor was operated at 30.0 ± 0.1°C. The recirculating solution flowrate was maintained at 152 $ml\,min^{-1}$, corresponding to a Reynolds number of 1250 at 30°C. The feed flowrate supplied to the recirculating solution reservoir was set at 7.3 $ml\,min^{-1}$. For a constant air flowrate of 0.40 $dm^3\,min^{-1}$, the membrane module temperature was increased stepwise from 30 to 50°C, and then to 60°C. The temperature increase led to a higher MCB load entering the bioreactor.

In the second set of experiments, the bioreactor was operated at 15.0 ± 0.1°C, with a volume of 1.0 l. The recirculating solution flowrate was maintained at 968 $ml\,min^{-1}$, corresponding to a Reynolds number of 7930 at 30°C. A constant MCB load entering the bioreactor was maintained in all experiments of this set (i.e. $C_{g,MCB}F_g$ = constant). To achieve this, as pervaporation temperature increased, the air flowrate and/or the feed solution flowrate were decreased accordingly. The combinations of temperature and air flowrate used throughout the second set of experiments are listed in Table 2. Each phase in this table corresponds to a time period of constant temperature and air flowrate.

In order to determine the overall mass transfer coefficients in the membrane module, an additional experiment at each of the three different temperatures 30, 50 and 70°C, was performed at a constant gas flowrate of 0.40 $dm^3\,min^{-1}$, using the membrane module only. This was done to confirm the values of the overall mass transfer coefficients and was performed at the

Table 2
Gas flowrate and temperature used in different sequential periods throughout the second set of experiments

Periods	T (°C)	F_g at STP ($dm^3\,min^{-1}$)
1, 3, 6, 8, 10	30	0.40
2, 4, 7	50	0.08
5	50	0.20
9	70	0.05

higher gas flowrate, as mass transfer coefficients are subject to larger error for the lower gas flowrates.

2.1. Chemicals

All chemicals used in the preparation of mineral medium were obtained from BDH (UK) and were of AnalaR grade. The organic solvents were obtained from Sigma (UK), and were >99% pure. All chemicals were used as supplied.

2.2. Analytical methods

MCB concentration was determined by gas chromatography in a Perkin-Elmer gas chromatograph with a flame ionisation detector (FID) and a megabore column 25 m long and 0.23 mm i.d. with BP1 (SGE, Australia) as the stationary phase. The temperature programme ran from 50°C to 140°C at a rate of 20°C min^{-1}. MCB in liquid samples was detected after extraction of the sample into a solution of dichloromethane with aniline as internal standard. 1 μl of the extracted sample was injected into the GC. MCB concentration in the gaseous phase was measured by withdrawing gas samples with a 1 ml gastight syringe and injecting directly into the GC. The coefficient of variation was 4.6% for the liquid assay at the 10 g m^{-3} level and 2.0% for the gas assay at the 4.0 g m^{-3} level.

Chloride concentration was measured by ion chromatography (Dionex 120, anion column AS14-4 mm, Germany). The eluent consisted of a 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$ solution, flowing at 1.11 ml min^{-1}. Prior to ion chromatography analysis, the biomedium samples were centrifuged (Haeareus, UK) at 12,000 rpm for 10 min, to remove biomass. The coefficient of variation was 5% at the 228 g m^{-3} level.

The 95% confidence interval has been calculated for the overall and membrane mass transfer coefficients, and for the removal efficiency of MCB in the bioreactor, as

$$\mathrm{IC}_{95\%} = \mu \pm t_{n-1,\alpha=0.05}\frac{\sigma}{\sqrt{n}} \quad (1)$$

where μ is the mean, σ the standard deviation, n the number of observations and t the critical t value, at 5% significance level for $(n-1)$ d.f..

3. Theory

Either concentration or partial vapour pressure can be used to describe mass transfer across membranes. The flux across the membrane can be expressed as

$$J_i = Q_{\mathrm{ov},i}A(p_{\mathrm{l},i} - p_{\mathrm{g},i}) = K_{\mathrm{ov},1}A(C_{\mathrm{l},i} - C^*_{\mathrm{g},i}) \quad (2)$$

where J_i is the flux of i across the membrane, $Q_{\mathrm{ov},i}$ the overall mass transfer coefficient of i in terms of vapour pressure, A is the membrane area, $p_{\mathrm{l},i}$ and $p_{\mathrm{g},i}$ are partial vapour pressures of i in the liquid side and in the permeate (or gas) side, respectively, $K_{\mathrm{ov,l}}$ the overall mass transfer coefficient of i in terms of liquid concentration, $C_{\mathrm{l},i}$ is the concentration of i in the liquid and $C^*_{\mathrm{g},i}$ the concentration of i in the liquid which would be in equilibrium with the gas. In pervaporation, the partial vapour pressure is preferred as a measure of the driving force [5,7], since the effects of temperature on the driving force and on the mass transfer coefficients are separated more clearly.

The partial vapour pressure of i in the liquid side is related to the concentration in the liquid side ($C_{\mathrm{l},i}$) by the expression

$$p_{\mathrm{l},i} = \frac{C_{\mathrm{l},i}\gamma_i P_i^0}{\rho_{\mathrm{l}}} \quad (3)$$

where γ_i is the activity coefficient of i in the liquid side, P_i^0 the saturation vapour pressure of pure i at the liquid temperature and ρ_{l} the molar density of the liquid. The partial vapour pressure of i in the gas side is related to the concentration in the gas side ($C_{\mathrm{g},i}$) by the expression

$$p_{\mathrm{g},i} = \frac{C_{\mathrm{g},i}P}{\rho_{\mathrm{g}}} \quad (4)$$

where P is the total pressure in the gas side and ρ_{g} the molar density of the gas.

The resistances-in-series model is commonly used to describe mass transfer in pervaporation, where the overall resistance to mass transfer is defined as the sum of the liquid boundary layer resistance and the membrane resistance (gas boundary layer resistance assumed negligible) [5]:

$$\frac{1}{Q_{\mathrm{ov}}} = \frac{1}{Q_{\mathrm{mem}}} + \frac{1}{Q_{\mathrm{l}}} = \frac{r_{\mathrm{in}}\ln(r_{\mathrm{ou}}/r_{\mathrm{in}})}{P_{\mathrm{mem}}} + \frac{\gamma P^0}{\rho_{\mathrm{l}}k_{\mathrm{l}}} \quad (5)$$

The liquid phase mass transfer coefficient for a driving force expressed in terms of vapour pressure (Q_l) is related to the liquid phase mass transfer coefficient for a driving force in terms of concentration (k_l) as follows:

$$Q_l = \frac{\rho_l}{\gamma P^0} k_l \tag{6}$$

The factor $\gamma P^0/\rho_l$ is the conversion factor from a concentration driving force to a partial vapour pressure driving force. It is useful to note this conversion factor since values for Q_l are not generally available, and it is k_l which is normally found in correlations which relate mass transfer coefficient to physical and hydrodynamic conditions. Similarly, to convert the overall mass transfer coefficient from a vapour pressure driving force (Q_{ov}) into a concentration driving force (K_{ov})

$$Q_{ov} = \frac{\rho_l}{\gamma P^0} K_{ov,l} \tag{7}$$

From a mass balance on the gas side of the membrane module, at steady-state, assuming the gas phase behaves as an ideal gas, and for constant molar flowrates, the following expression determines the overall mass transfer coefficient:

$$Q_{ov} = -M \frac{1}{(M/N) - 1} \ln \left[\frac{p_l}{\{(M/N) - 1\} p_g + p_l} \right] \tag{8}$$

where

$$M = \frac{F_g}{RT} \tag{9}$$

and

$$N = \frac{F_l \rho_l}{\gamma P^0} \tag{10}$$

The activity coefficient of MCB was approximated by the activity coefficient at infinite dilution and estimated by the inverse of the solubility (expressed as a mole fraction), a method commonly used and valid for organic compounds that are sparingly soluble in water [21]. MCB saturation vapour pressure [22] and activity coefficient at infinite dilution [23] at the temperatures studied are listed in Table 3.

The liquid phase mass transfer coefficient k_l may be estimated by dimensionless correlations. For turbulent conditions, which prevailed throughout the experiment, the following correlation [24] may be used to estimate k_l:

$$Sh = 0.026 Re^{0.8} Sc^{0.33} \tag{11}$$

Table 3
Saturation vapour pressure and activity coefficient at infinite dilution for MCB at different temperatures

T (°C)	P^0 (Pa)	γ
30	2060	11587
50	5597	7077
60	8738	5388
70	13052	4136

From Q_{ov} determined experimentally and k_l estimated from Eq. (11), and using Eq. (5), the membrane mass transfer coefficients were determined. The permeability through the membrane, P_{mem}, is usually described by the solution–diffusion model [25], as the product of the diffusivity through the membrane and the solubility in the membrane. Diffusion coefficients increase with the temperature, while sorption is usually exothermic [25–27]. Different results have been reported in the literature for the effect of temperature on the permeability of organic compounds through a membrane, some where permeability decreases with temperature [26,27], others where permeability increases with temperature [10], and others where permeability is unaffected by temperature within the range studied [5,16].

4. Results and discussion

4.1. Pervaporation unit: effect of temperature on mass transfer

The overall mass transfer coefficient of MCB through silicone rubber, the liquid phase mass transfer coefficient and the membrane mass transfer coefficient, all based on a partial vapour pressure driving force, are shown as a function of temperature in Fig. 2. The overall mass transfer coefficient can be seen to be constant over the range of temperature studied, at 1.4×10^{-7} mol m^{-2} Pa^{-1} s^{-1}.

The effect of temperature on k_l, which is apparent in Fig. 3, is derived from changes in the physical properties of the solution, mainly its viscosity. For

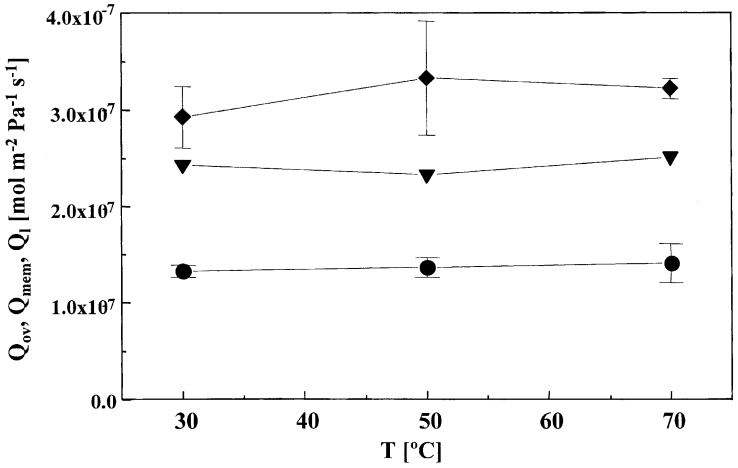


Fig. 2. Overall mass transfer coefficient (●); membrane mass transfer coefficient (◆); and liquid mass transfer coefficient (▼) for a partial vapour pressure driving force basis, as a function of temperature. 95% confidence intervals are shown for the overall and the membrane mass transfer coefficients.

the same flowrate, the Reynolds number increases strongly with temperature. From 30°C at a constant liquid flowrate, the Reynolds number increased from 7930 to11469 at 50°C and to 15573 at 70°C. In terms of the overall mass transfer coefficient, however, the effect of increased temperature on k_l was cancelled out by the increase in the saturation vapour pressure P^0 (Q_l constant with T, Fig. 2). The liquid boundary layer

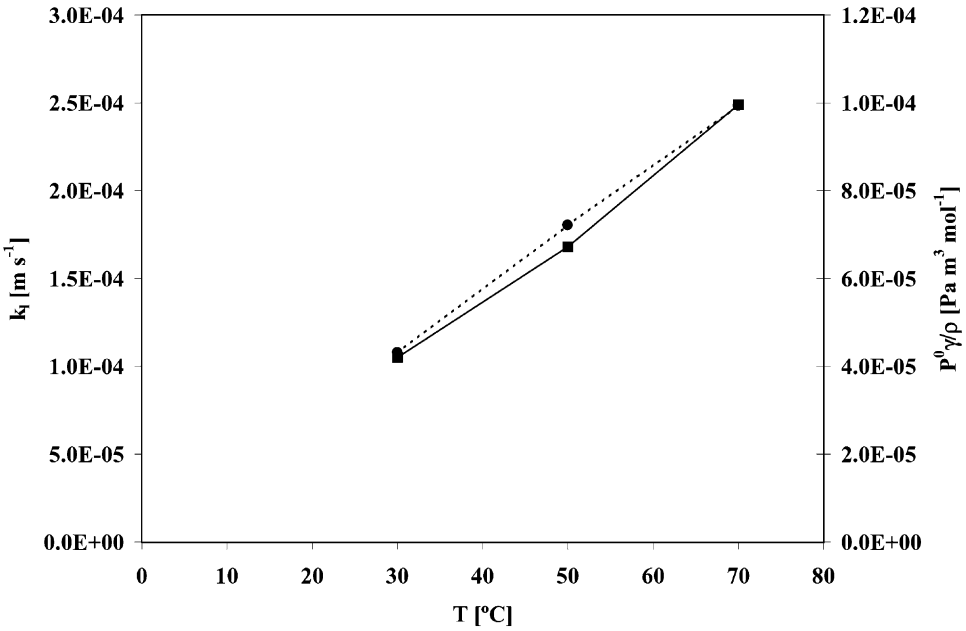


Fig. 3. Liquid mass transfer coefficient based on concentration driving force (■) and conversion factor from concentration to partial vapour pressure driving force (●), as a function of temperature.

resistance ($1/Q_l$) accounted for about 57% of the total resistance to mass transfer ($1/Q_{ov}$), the remainder being due to the membrane resistance.

From the experimentally determined overall mass transfer coefficient, with k_l estimated from a Sherwood correlation for turbulent conditions (Eq. (11)) and using the resistances-in-series model (Eq. (5)), Q_{mem} was determined. This was shown to be constant with temperature over the range studied. This result is consistent with the results of Baudot and Marin [16], who state that the permeability of organophilic membranes was negligibly affected by changes in feed temperature. The intrinsic vapour permeability of the membrane, P_{mem}, had an average value of 2.4×10^{-10} mol m m^{-2} s^{-1} Pa^{-1}. This value is approximately 3.8 times higher than a value determined at 25°C for MCB crossing PDMS by Raghunath and Hwang [28]. However, no details of the membrane used for the Raghunath and Hwang study were given and the difference may be due to differences in the membrane material.

4.2. Bioreactor operating at 30°C: constant air flowrate entering the bioreactor (first set of experiments)

The results for the first set of experiments are presented in Table 4. The gas outlet from the bioreactor was in thermal equilibrium with the biomedium throughout the experiment.

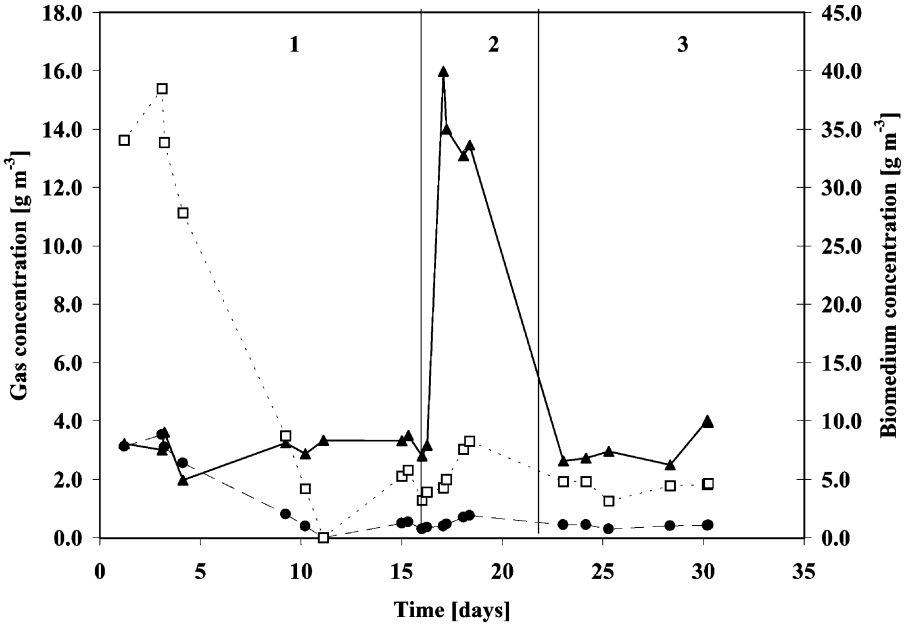
For a constant air flowrate, the beneficial effect of increasing temperature on the mass transfer of MCB across the membrane was reflected in an increase of the MCB concentration in the air stream leaving the membrane module, as can be seen in Table 4. For an increase in temperature from 30°C to 50°C, the MCB concentration in the gas outlet of the membrane module (at standard temperature and pressure) increased by a factor of 1.3, from 3.2 to 4.2 g m^{-3}. From 30 to 60°C, the increase was by a factor of 1.6.

A corresponding increase in the elimination capacity of the bioreactor accompanied the increase in the MCB load into the bioreactor. An elimination capacity of 84 g (MCB) m^{-3} h^{-1} was attained in this experiment, for an inlet concentration in the air stream of 5.2 g m^{-3}. It was observed that the removal efficiency of the bioreactor was maintained at a very high level throughout the experiment, close to 100% removal efficiency, indicating that the system was limited by mass transfer in the pervaporation module. Removal efficiency results were confirmed by chloride analysis. No effect on the removal efficiency in the bioreactor could be detected when pervaporation operating conditions were altered.

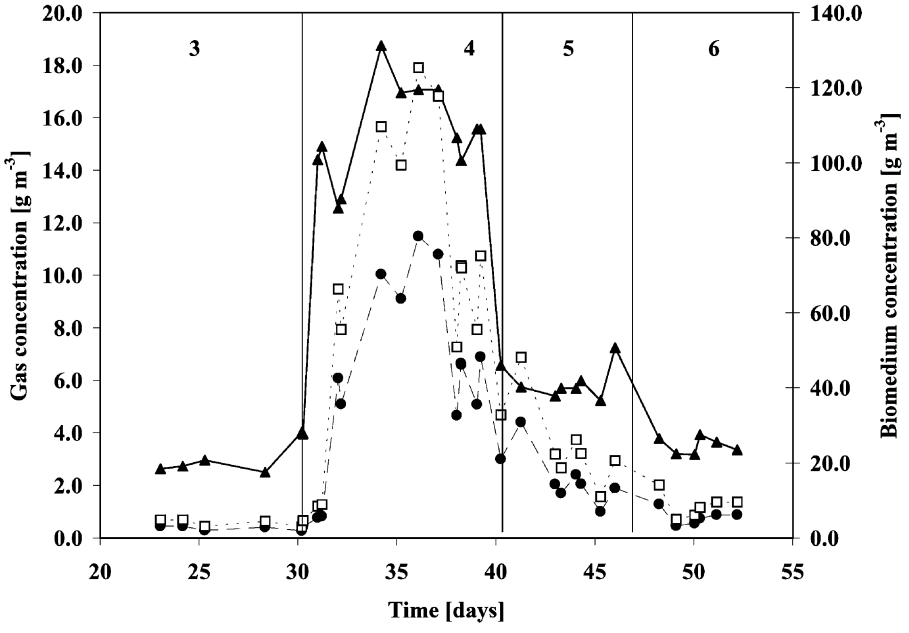
In order to establish a better understanding of the effects of using higher pervaporation temperatures on the bioreactor performance, it was necessary to run the system under conditions where improvements, if any occurred, could be quantified. Under the conditions employed in the first set of experiments, with MCB removals across the bioreactor of 99.8–100%, it was impossible to detect whether decreasing the gas flowrate and increasing MCB concentration in the inlet gas to the bioreactor would exert a positive effect. Higher loads of MCB needed to be entering the bioreactor to result in removals across the bioreactor in the range of 80–100%. This was difficult to achieve experimentally, as it would imply the handling of high volumes of MCB feed solution or the use of a very large membrane module with subsequently high feed and air flowrates. Slowing down the microbial activity was decided upon as an alternative, and a second set of experiments was performed with the bioreactor operating at a lower temperature (15°C). Additionally, the bioreactor volume was decreased to 1 l.

Table 4
Gas concentration at the gas outlet of the membrane module (at STP), MCB load into the bioreactor, MCB elimination capacity (per bioreactor volume) and removal efficiency of the bioreactor, at steady-state, for the three pervaporation temperatures studied in the first set of experiments

T (°C)	Gas concentration (g m^{-3})	Load (g m^{-3} h^{-1})	EC (g m^{-3} h^{-1})	Removal efficiency (%)
30	3.2	51.7	51.7	99.9
50	4.2	67.0	66.9	99.8
60	5.2	83.8	83.8	100.0

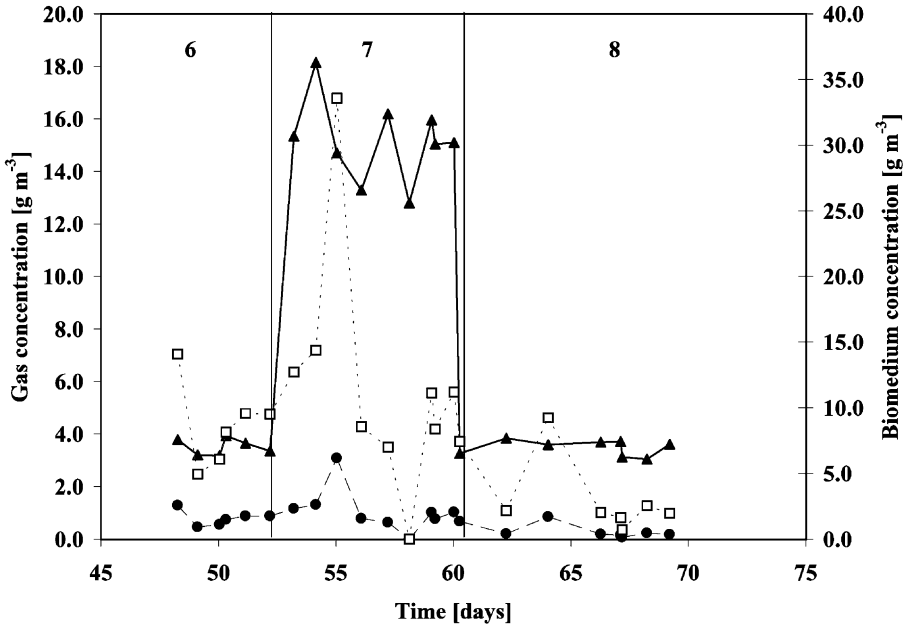


(a)

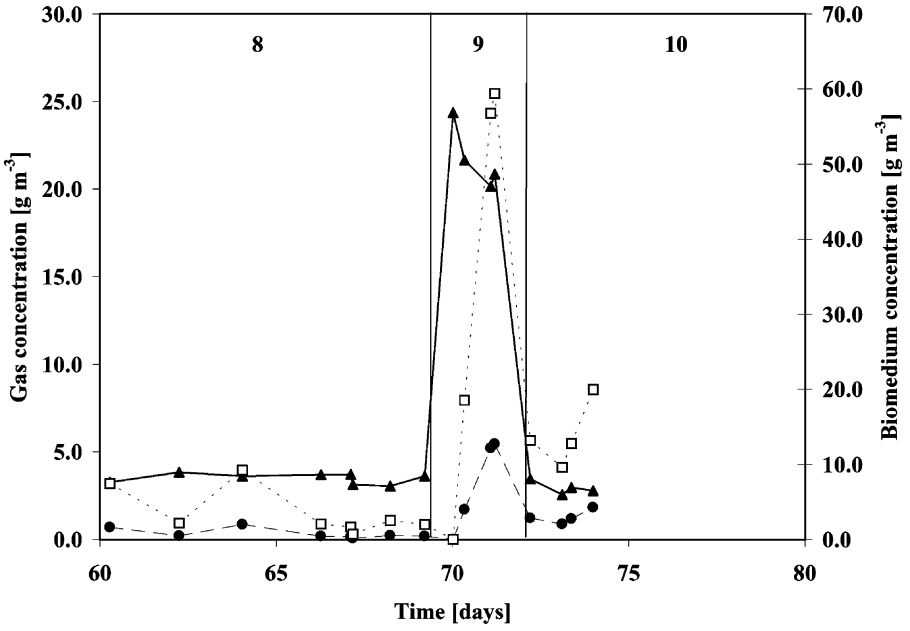


(b)

Fig. 4. (a) Concentrations of MCB in the bioreactor: at the gas inlet (▲); at the gas outlet (●); and in the biomedium (□) for the first cycle 30, 50, and 30°C (cycle corresponding to periods 1–3, second set of experiments). (b) Concentrations of MCB in the bioreactor: at the gas inlet (▲); at the gas outlet (●); and in the biomedium (□) for the second cycle 30, 50, and 30°C (cycle corresponding to periods 3–6, second set of experiments). (c) Concentrations of MCB in the bioreactor: at the gas inlet (▲); at the gas outlet (●); and in the biomedium (□) for the third cycle 30, 50, and 30°C (cycle corresponding to periods 6–8, second set of experiments). (d) Concentrations of MCB in the bioreactor: at the gas inlet (▲); at the gas outlet (●); and in the biomedium (□) for the cycle 30, 70, and 30°C (cycle corresponding to periods 8–10, second set of experiments).



(c)



(d)

Fig. 4. (*Continued*).

4.3. Bioreactor operating at 15°C: constant MCB load entering the bioreactor (second set of experiments)

The concentrations of MCB in the gas inlet and outlet of the bioreactor, and those in the biomedium, for all conditions studied during this experiment, are shown in Fig. 4a–d. Three cycles of temperature, changing stepwise from 30 to 50°C and back to 30°C, were run during the experiment (Fig. 4a–c), as well as one run where the temperature was changed from 30 to 70°C (Fig. 4d). The gas outlet from the bioreactor was in thermal equilibrium with the biomedium throughout the experiment. The removal of MCB in the bioreactor due to microbial degradation over the full range of conditions studied is shown in Fig. 5.

The results in Fig. 4a (periods 1–3) show that the bioreactor dealt effectively with the temperature and subsequent gas concentration increases, keeping the concentration of MCB at the gas outlet at a low level ($0.6\,g\,m^{-3}$), with increased removal efficiency, from 87 to 95% (shown in Fig. 5). It is important to note that the load into the bioreactor was kept the same throughout, resulting in the MCB concentration in the gas increasing from 3.4 to about $16.7\,g\,m^{-3}$ for the temperature rise 30 to 50°C.

When repeating the change of conditions (periods 3–6), Fig. 4b shows a different bioreactor behaviour. The MCB initially accumulated in the biomedium, and the removal in the bioreactor decreased significantly to a stable value, much lower than that obtained for the first cycle. Hypothesising that increased MCB concentration in the gas inlet was leading to an inhibitory liquid phase concentration, the gas flowrate was increased from 0.08 (period 4) to $0.20\,dm^3\,min^{-1}$ (period 5). However, the removal remained lower than that obtained for the first cycle.

In the third trial (Fig. 4c, periods 6–8), an initial increase of the concentration in the biomedium was observed, but the bioreactor soon responded and the removal increased to the level observed in the first trial (see Fig. 5).

An improvement in the bioreactor performance is observable in two of the three trials. The percentile

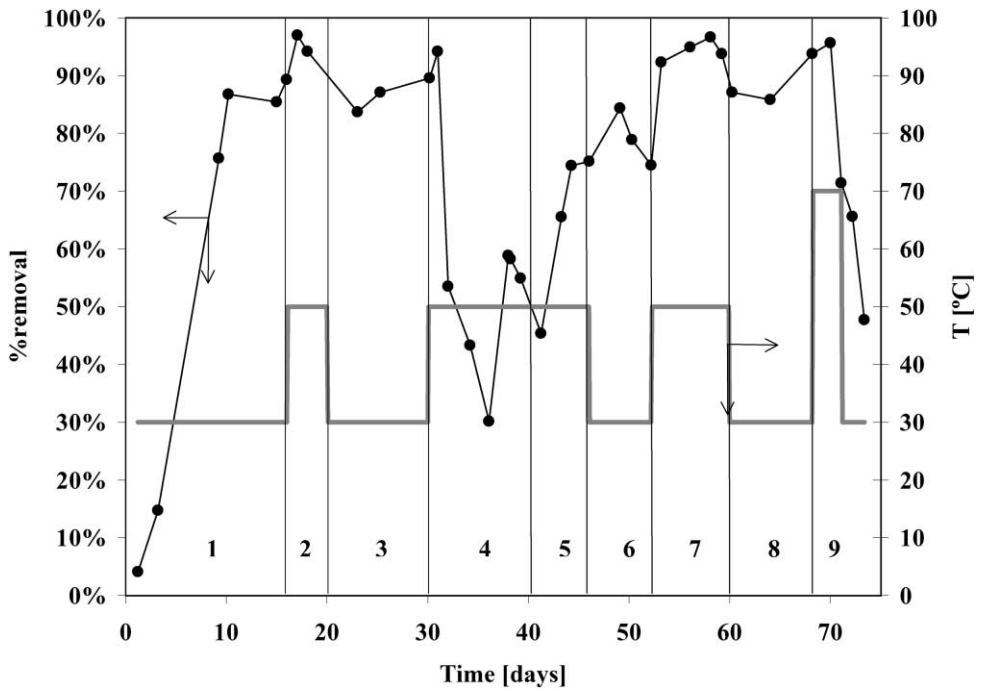


Fig. 5. Percentage removal of MCB in the bioreactor due to microbial degradation and temperature of the gas stream entering the bioreactor during the second set of experiments.

removal increased from 87 ± 3% with a gas flowrate of 0.40 $dm^3\,min^{-1}$ at 30°C, to 95 ± 2% with a gas flowrate of 0.08 $dm^3\,min^{-1}$ at 50°C. It may be that in the second trial, due to slight oscillations in the load of MCB into the bioreactor at the relatively high inlet concentration, the microorganisms did not respond promptly and this led to an accumulation of MCB in the biomedium. The higher concentration in the biomedium may have become inhibitory and the system was unable to recover. *Pseudomonas* sp. strain JS150 has been found to be strongly inhibited at MCB concentrations higher than 160 $g\,m^{-3}$ (liquid phase concentrations), for operation at 30°C [29]. At 15°C, the concentration of MCB that becomes inhibitory may be lower, explaining the observed behaviour.

The results in Fig. 4d show that, on changing the gas temperature from 30 to 70°C (periods 8–9), a rapid increase of MCB concentration in the biomedium and a simultaneous decrease in the bioreactor removal efficiency occurred. It appears that due to the very high MCB gas concentration entering the bioreactor (27 $g\,m^{-3}$), the increase in MCB mass transfer rate from the gas into the biomedium was such that the bioreactor was unable to respond sufficiently rapidly. This illustrates a limitation of this system, as bioreactors are known not to cope with shock loading easily. Rather than implementing rapid changes in operating conditions, the conditions should be changed smoothly so that the increase in the gas inlet concentration does not result in an inhibitory accumulation in the liquid phase.

Fig. 6 shows the evolution of chloride ion concentration expected from stoichiometric consideration of the amount of MCB removed from the waste gas, and measured experimentally as chloride in the biomedium. There is good agreement between the expected values and the measured values, showing that MCB removed from the gas was biodegraded.

The use of a lower gas flowrate will decrease the mass transfer coefficient for the transfer of the VOC from the gas into the liquid in the bioreactor. For a stirred tank, the $k_l a$ depends on the gas flowrate to an exponent of 0.2 [30]. However, the positive effects of higher concentration and cooling are expected to be

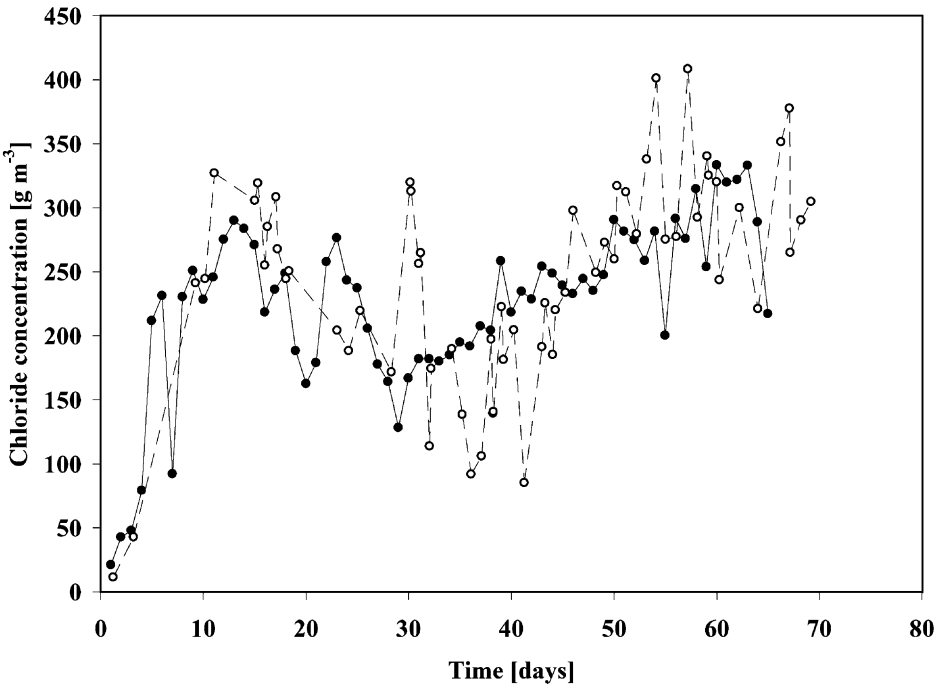


Fig. 6. Chloride ion concentration in the bioreactor: measured values (●) and expected values (○). The expected values were calculated assuming complete mineralisation of MCB.

considerably more significant than the negative effects of the small decrease of $k_l a$ with the decrease of the gas flowrate. From examining the results of this study in their entirety (Fig. 6), it is clear that the mass transfer from the gas into the liquid indeed increased when the temperature and gas flowrate was changed from 30°C and 0.40 $dm^3\,min^{-1}$ to 50°C and 0.08 $dm^3\,min^{-1}$, respectively. These results show that the system was mass transfer limited in the pervaporation module at its initial conditions.

An elimination capacity of 73 g (MCB) $m^{-3}\,h^{-1}$ was obtained in the bioreactor working at a temperature of 15°C. With decreasing gas flowrate and increasing temperature, an improvement was obtained. The elimination capacity of the bioreactor increased from 73 to 79 g (MCB) $m^{-3}\,h^{-1}$, for the same operation temperature in the bioreactor.

Mpanias and Baltzis [20] reported elimination capacities of a biotrickling filter removing MCB from a gas stream between 5.6 and a maximum of 60 g (MCB) m^{-3} h^{-1} reactor. Their operating temperature was 25°C. Their removal efficiencies varied between 94% (EC = 6.7 g (MCB) $m^{-3}\,h^{-1}$ reactor) and 68% (EC = 26.8 g (MCB) h^{-1} reactor), depending on the inlet concentration in the gas and recirculating liquid flowrate. Oh and Bartha [31] report an elimination of 5.1 g (MCB) $m^{-3}\,h^{-1}$ also in a biotrickling filter operating at 20–25°C. Although it is difficult to compare a CSTR with biotrickling filters simply by direct comparison of the elimination capacities per volume of bioreactor, it is clear that the values obtained in this work were significantly higher, especially considering the differences in the operating temperatures.

5. Conclusions

- An increase in the pervaporation gas temperature increased the mass transfer of MCB due to its strong effect on the driving force; the overall mass transfer coefficient was shown to be constant across the temperature range investigated. Such a temperature rise will thus allow a reduction in the membrane area necessary for the same VOC removal.
- The bioreactor efficiently eliminated the MCB from the contaminated air stream resultant from the pervaporation process. Removal efficiencies of approximately 100% were observed throughout the experiment, for increasing MCB load entering the bioreactor, in a bioreactor operating at 30°C. An elimination capacity of 84 g (MCB) $m^{-3}\,h^{-1}$ was observed in the bioreactor.
- The higher the temperature, the higher the saturation concentration of the VOC in the gas, and thus the lower the gas flowrate which may be used for the same removal.
- Using a lower gas flowrate at a higher temperature increased the removal efficiency of the bioreactor. More MCB was transferred to the liquid phase, and the microorganisms were able to degrade it, showing that the system was mass transfer limited at the initial conditions.
- Gas concentrations of 17 g m^{-3} were treated in a bioscrubber at 15°C with removals of 95%. An average elimination capacity of 79 g (MCB) $m^{-3}\,h^{-1}$ was observed for a bioreactor operating at 15°C. This is a high elimination capacity for the biodegradation of a chlorinated compound, particularly considering the low operating temperature of the bioreactor.
- The system appeared sensitive to shock loadings. It may be necessary to ensure smooth transitions in the VOC concentration of the inlet gas during changes in operating conditions.

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