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An Oil-Absorber−Bioscrubber System To Stabilize Biotreatment of Pollutants Present in Waste Gas. Fluctuating Loads of 1,2-Dichloroethane

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Biotreatment technologies offer a cost-effective and efficient method for dealing with point-source releases of solvents. However, a major problem hampering these technologies is the fluctuating pollutant loads, which is especially critical for inhibitory pollutants. Provision of biotreatment systems able to cope with this problem is a significant technological and environmental challenge. This study investigates the potential for an absorber to act as buffer for shock loadings of inhibitory pollutants in waste-gas streams undergoing biological treatment. 1,2-Dichloroethane (DCE) was used as an example of a toxic and inhibitory organic pollutant. The stability of a combined oil-absorber−bioscrubber (OAB) system was compared to that of a bioscrubber only (BO) system when each was subjected to shock loads of DCE. The BO system was inoculated with *Xanthobacter autotrophicus* strain GJ10 and was submitted to sharp, sequential pulses in DCE inlet load, which caused system instability. Complete inhibition of the BO process occurred for a 3 h DCE pulse, leading to 9125 g of DCE $m^{-3}_{bioscrubber}$ total organic discharged (TOD_{DCE}). Following the pulse, fluorescence in situ hybridization (FISH) showed that the active strain GJ10 was effectively washed-out. In contrast, the performance of the OAB system was stable during DCE shock loads. The carbon dioxide production remained stable, and low levels of effluent DCE and total organic carbon concentrations were found. For the 3 h pulse TOD_{DCE} was only 173 g of DCE $m^{-3}_{bioscrubber}$, and FISH indicated that the GJ10 strain remained active. We conclude that the OAB system offers an effective solution to the biological treatment of waste-gas containing fluctuating pollutant concentrations.

Introduction

Processes for biological treatment of pollutants can be exposed to dynamic pollutant loadings when applied in situ (*1*), including peak concentration levels of toxic compounds produced from batch cycles. Shock loads of inhibitory compounds may cause instability of the biological process, may cause perturbation between steady states (*2*), or may make steady-state operation impossible (*3*). Various studies have also shown that high concentrations of inhibitory compounds may cause inhibition or even failure of the biological process (*4*−*7*). A few examples of reversible and nonreversible performance deterioration due to sudden increases in the pollutant loading rate for different waste-gas biotreatment systems are summarized in Table 1. This suggests a need for robust technologies to control concentration of inhibitory compounds prior to biological treatment.

Different bioreactor designs and control strategies have been proposed to address this challenge. Immobilized cells, such as aerobic granules (*8*−*10*) or wall growth (*4*, *11*), have been suggested to prevent inhibition or wash-out during transient bioreactor operation. Yeom and Yoo (*12*) proposed a hybrid bioreactor comprised of a bubble column for removal of influent benzene by immobilized cells and a biofilter for treatment of the air-stripped benzene. Al-Ryes et al. (*13*) tested a dampening system consisting of an absorption column, utilizing water as the scrubbing liquid and a mass equalization tank. This system, though, could only dampen short-term fluctuations of water soluble compounds, so the addition of an organic solvent to the scrubbing water was required. The use of granular activated carbon (GAC) has also been reported for controlling fluctuating substrate concentrations. A mixture of GAC and compost was successfully applied to enhance the performance of a biofilter subjected to shock loadings of BTEX (benzene, toluene, ethylbenzene, and *o*-xylene) (*14*). Weber and Hartmans (*15*) used a GAC column in series with a biofilter to control fluctuating toluene concentrations in the feed stream to the biofilter. Solid polymers have recently been applied for the adsorption of organic substrates (*16*, *17*). Daugulis et al. (*17*) used two different polymers for benzene adsorption and delivery to a bioreactor and suggested that modified polymers may provide the development of delivery systems with desirable physical properties.

The use of an organic phase as an absorbent for inhibitory pollutant concentrations has been applied in two phase partitioning bioreactors (TPPBs) (*18*, *19*). TPPBs have been used for the degradation of xenobiotic compounds in batch, fed-batch, and continuous bioreactor applications, achieving high degradation rates, either utilizing a scrubber unit as an absorber (*20*, *21*) or in direct contact two-phase systems (*22*−*27*). However, in all TPPB studies presented above, the organic phase used has to be biocompatible, to be nonbiodegradable, and to give acceptable phase separation. A system able to exploit biodegradable or nonbiocompatible solvents for dampening fluctuating pollutant loads in the bioreactor was proposed by Oliveira and Livingston (*7*). They used a silicone oil absorber placed upstream to the bioreactor, thus keeping the two phases separate. In this way, phase separation was not required and there were fewer constraints for the selection of absorbent.

This work investigates the operational stability that an absorber with sunflower oil as absorbent liquid provides to a bioscrubber subjected to shock loads of 1,2-dichloroethane (DCE) in a waste gas. Sunflower oil was chosen because of its high partition coefficient for DCE, low volatility, and low cost. The absorber alone was first studied experimentally and through a mathematical model, to understand how to size it so that inlet DCE loads would be effectively smoothed out. The stability of the oil absorber bioscrubber (OAB) was compared with the bioscrubber only (BO) system when challenged with the same shock loads of DCE. Microbial culture dynamics was monitored during the experiments using fluorescence in situ hybridization (FISH).

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TABLE 1. Performance Deterioration for Different Waste Gas Biotreatment Systems Due to Sudden Increases in the Pollutant Loading Rate

		loading rate ($g\ m^{-3}\ h^{-1}$)		
inhibitor	biotreatment system	initial loading rate	increased loading rate	stated effects
monochlorobenzene (2)	bioscrubber	19.2	91.2	removal efficiency dropped from 95% to 30%
monochlorobenzene (7)	bioscrubber	690	1100	wash-out
phenol (5)	activated sludge process	12.5	83.3	process break-down
phenol (6)	activated sludge process	41.7	62.5	process break-down

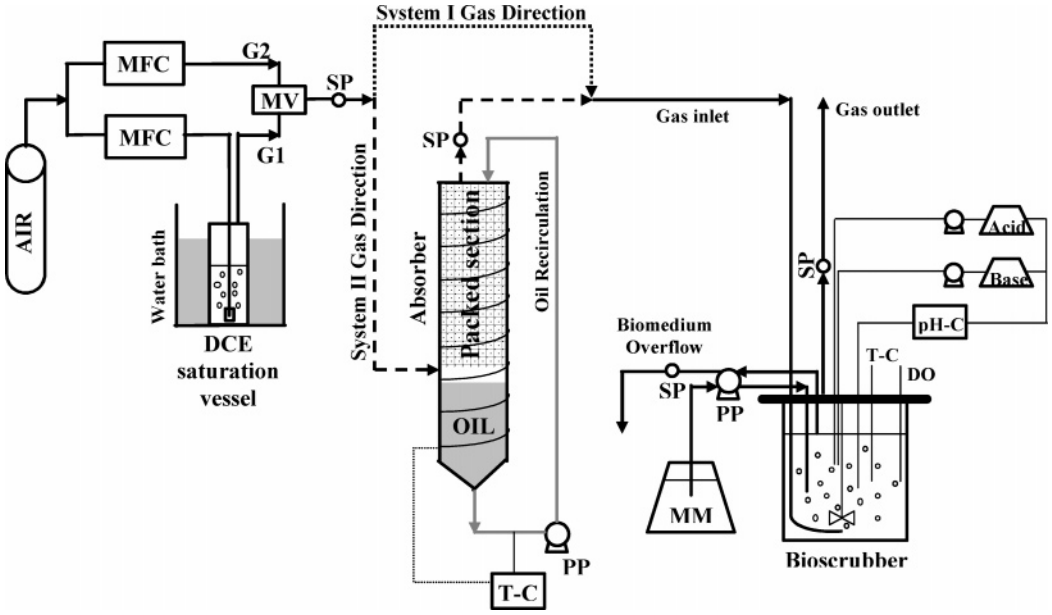

FIGURE 1. Schematic of the experimental setup: System I gas direction was followed when the gas bypassed the absorber and was introduced directly to the bioscrubber. For system II gas direction the gas passed through the absorber and then was fed to the bioscrubber. DO, dissolved oxygen meter; G1, G2, gas streams (total air flow rate: 0.3 L min^{-1}); MFC, mass flow controller; MM, mineral medium (dilution rate: 0.053 h^{-1} for 1.5 L bioscrubber working volume); MV: mixing vessel; pH-C, pH controller; PP, peristaltic pump (sunflower oil recirculation rate, 2 L min^{-1}); SP, sampling port; T−C, temperature controller (temperature was maintained at 30 °C).

Experimental Section

Microorganism and Mineral Medium. Subcultures of *Xanthobacter autotrophicus* GJ10 (ATCC no. 43050) were grown in mineral medium containing 200 g m^{-3} DCE, incubated at 30 °C, and used for bioscrubber inoculation. The composition of the mineral medium was 1360 g m^{-3} KH_2PO_4, 2130 g m^{-3} Na_2HPO_4, 3000 g m^{-3} $(NH_4)_2SO_4$, 200 g m^{-3} $MgSO_4{\cdot}7H_2O$, 5 L m^{-3} trace elements solution (*28*), and 1 L m^{-3} vitamin solution (*28*).

Experimental Setup. The experimental setup is shown in Figure 1. When DCE pulses were introduced directly to the bioscrubber, the absorber was not used and the gas stream followed system I gas direction. During the initial experiments investigating the absorber alone, the bioscrubber was not connected. A detailed description of the experimental setup can be found as Supporting Information (page S-1).

Chemicals. All chemicals used were obtained from Merck (U.K.) and were of ANALAR grade. DCE was obtained from Sigma (U.K.) 99% pure.

Analysis. Gas chromatography (GC) analysis was employed for determination of the DCE concentration in the gaseous and aqueous samples. The coefficient of variation for five samples was 0.2% at a concentration level of 24 g_{DCE} m^{-3}.

Carbon dioxide concentration of the bioscrubber gas effluent was determined using an isothermal GC. The coefficient of variation for five samples was 2.6% at a concentration level of 0.03% v/v carbon dioxide.

Biomass concentration was determined by absorbance at 660 nm on a UV−vis spectrophotometer (UNICAM) interpolating from a previously established dry weight calibration curve. The coefficient of variation for five samples was 2.3% at a concentration level of 0.5 $g_{biomass}$ m^{-3}.

Total organic carbon (TOC) was measured by a Shimadzu 5050 analyzer. The coefficient of variation for five samples was 0.5% at a concentration level of 500 g_{carbon} m^{-3}. More details about the analytical methods used can be found as Supporting Information (page S-2).

Partition Coefficient. The air−oil partition coefficient of DCE ($P_{i,oil}$) was determined for a range of different oils, using eq 1 (see page S-3, Supporting Information):

$$P_{i,\mathrm{oil}} = \frac{C_{i,\mathrm{oil}}}{C_{\mathrm{G,DCE}}} \quad (1)$$

Bacterial Population Analysis. The GJ10 specific oligonucleotide probe [5′CACCAACCTCTCTCGAACTC-3′] was used to identify GJ10 cells within the microbial community. The probe targeting the 16S rRNA was designed using Primrose computer software (29) and labeled at the 5′end with Cy3 fluorochrome (Thermo Electron GmbH, Germany). DAPI (4′, 6-diamidino-2-phenylindole) was used for determining the total number of cells present. Propidium iodide (PI), which is membrane impermeable and is generally excluded from viable cells, was used for identifying dead cells in the population. The slides were analyzed using

epifluorescence microscopy. A detailed description can be obtained from the Supporting Information (page S-4).

Results and Discussion

1. Oil-Absorber Design. *Absorbent Choice.* A range of potential absorber oils were selected for testing as an absorbent fluid based on physical, environmental, operational, and economic criteria. Desirable characteristics include low volatility, low-toxicity, potentially high partition coefficient for DCE, and low cost. Silicone oil and *n*-hexadecane were selected because they have been applied successfully in the past to control fluctuating concentrations of organics (*7*, *21*, *24*, *26*, *27*). Previous studies also found that environmentally friendly alternatives, such as vegetable oil, are effective for absorption of chlorinated organics (*30*); thus parafin oil and sunflower oil were also tested. The DCE partition coefficients are summarized together with the oil cost. These data are available in the Supporting Information (Table S-1). Sunflower oil was selected for application in the absorber due to the fact that it exhibited the highest partition coefficient for DCE (652), it is environmentally friendly, and it is the most cost-effective.

The temperature dependence of the sunflower oil DCE partition coefficient was determined experimentally (data not shown) to be linear for a temperature range between 20 and 52 °C and is expressed by eq 2:

$$P_{\text{sun,oil}} = -12.1T + 1049.6 \quad (2)$$

where $P_{\text{sun,oil}}$ is the partition coefficient for DCE between sunflower oil i and air [−] and T is the absorber temperature [°C].

This dependence suggests the potential for future work of varying the temperature of the oil to control the absorption or desorption of pollutant. During periods of high substrate load the temperature of the oil might be decreased to absorb higher amounts of pollutant, while during starvation periods it can be increased to desorb the pollutant and maintain the bacterial culture in the bioreactor active.

Oil-Absorber: Comparison between Experimental and Modeling Results. A mathematical model of the absorber was developed and is presented as Supporting Information (Pages S5, 6). Simulations were run for different oil volumes in order to estimate the volume required to sufficiently dampen the inhibitory DCE load. A comparison between the experimental and modeling results was performed for two different DCE pulses and for different oil volumes in the absorber (Figure 2). We introduced 0.3 L of sunflower oil to the absorber, and a DCE contaminated gas stream with an inlet concentration of 24 g m^{-3} was fed continuously. When the system reached steady state, the inlet DCE concentration was increased to 44 g m^{-3} for 3 h and then decreased to the initial concentration level. The absorber outlet DCE concentration during the pulse reached a maximum value of 26 g m^{-3}, i.e., only 8% higher than the average outlet concentration before the introduction of the pulse (24 g m^{-3}). Under the same conditions, the simulations of the model calculated a maximum outlet DCE concentration of 29 g m^{-3} (21% increase). The excess mass of DCE fed during the 3 h period was 1.13 g. From this amount, 1.08 g was absorbed into the sunflower oil and, according to the model, should have desorbed over a time period of 3 days. A further and larger DCE pulse was introduced to the absorber containing 0.45 L of sunflower oil. In this experiment the DCE concentration at the absorber inlet was increased from 28 to 61 g m^{-3} for 6 h. During the pulse, the DCE concentration in the absorber outlet reached a maximum value of 38 g m^{-3}, which was 27% higher than the average concentration before the introduction of the pulse (30 g m^{-3}). The model estimated that the maximum outlet DCE concentration during the pulse should be 40 g m^{-3} (33% increase).

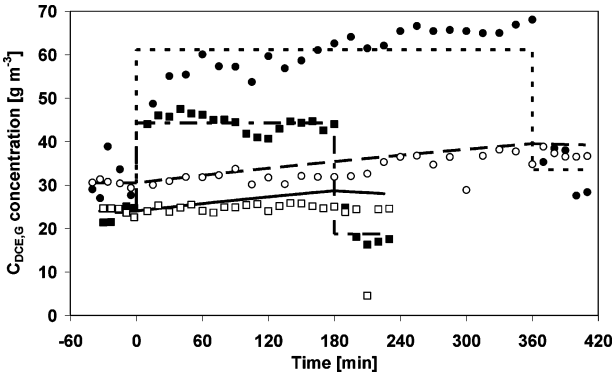

FIGURE 2. Comparison between experimental data and model predictions for experiments with absorber only (no bioscrubber). Time 0 indicates the beginning of the pulse. $C_{DCE,G}$ is the DCE concentration in the gas phase. For 3 h pulse (V_{oil}: 0.3 L): ■ $C_{DCE,G}$ inlet, experimental; □ $C_{DCE,G}$ outlet, experimental; — · — $C_{DCE,G}$ inlet, imposed; — $C_{DCE,G}$ outlet, predicted. For 6 h pulse (V_{oil}, 0.45 L): ● $C_{DCE,G}$ inlet, experimental; ○ $C_{DCE,G}$ outlet, experimental; ··· $C_{DCE,G}$ inlet, imposed; — — $C_{DCE,G}$ outlet, predicted.

These comparisons indicate that the experimental and modeling results for the two experiments performed are in fair agreement. During the 6 h period the excess DCE fed was 5.59 g, of which 5.31 g was absorbed into sunflower oil, and the model calculated that the excess DCE subsequently desorbed over a time period of 4 days.

The above results confirmed that the absorber containing 0.3−0.45 L provided sufficient dampening of the excessive DCE fed, and sharp increases of the DCE concentration in the process inlet were significantly reduced, as was predicted by the model estimations.

2. System I: Bioscrubber Only (BO). For system I experiments the absorber was not connected and the DCE pulses were introduced directly to the bioscrubber, operating at steady state with DCE removal higher than 90%.

Pulse I.1. A DCE pulse was introduced to the bioscrubber for 1 h. During the pulse, the inlet DCE concentration was increased from an average value of 15 to 207 g m^{-3} for 1 h and then was decreased to 14 g m^{-3}. The inlet DCE load to the bioscrubber increased from 183 to 2483 g m^{-3} h^{-1} and then decreased to 167 g m^{-3} h^{-1} (Figure 3A). Note that all the loads used in this work are calculated per m^3 of bioscrubber. Such a sharp increase of the DCE inlet load resulted in accumulation of DCE in the biomedium (Figure 3D). Ferreira Jorge and Livingston (*31*) reported that biomedium DCE concentrations above 1000 g m^{-3} cause total inhibition of GJ10 growth. DCE concentration reached an inhibitory level of 1084 g m^{-3} 0.5 h after the introduction of the shock load, and increased further to 1437 g m^{-3} by the end of the pulse. Although the microbial culture was exposed to inhibitory DCE concentrations, the biomedium concentration decreased, due to the volatility of DCE, to 496 g m^{-3} 1 h after the pulse and to 63 g m^{-3} after 2.3 h. Other process parameters also indicate that the system was unstable during the shock load. The TOC concentration in the biomedium increased from 0 g m^{-3} before the pulse to 587 g m^{-3} at the end of the pulse. The maximum TOC concentration that is deduced from the DCE concentration in the biomedium was ∼348 g m^{-3}. Strain GJ10 is known to produce extracellular polysaccharides when exposed to stress (*1*); thus the difference in the TOC could be due to these products and/or some intermediates from incomplete DCE degradation. The outlet DCE load of the bioscrubber increased from an average value of 17 g m^{-3} h^{-1} before the pulse to a maximum value of 1228 g m^{-3} h^{-1} at the end of the pulse. This resulted in a TOD_{DCE} of 1897 g $m^{-3}_{bioscrubber}$ (Figure 5). Furthermore, the carbon dioxide concentration of the gas effluent did not increase

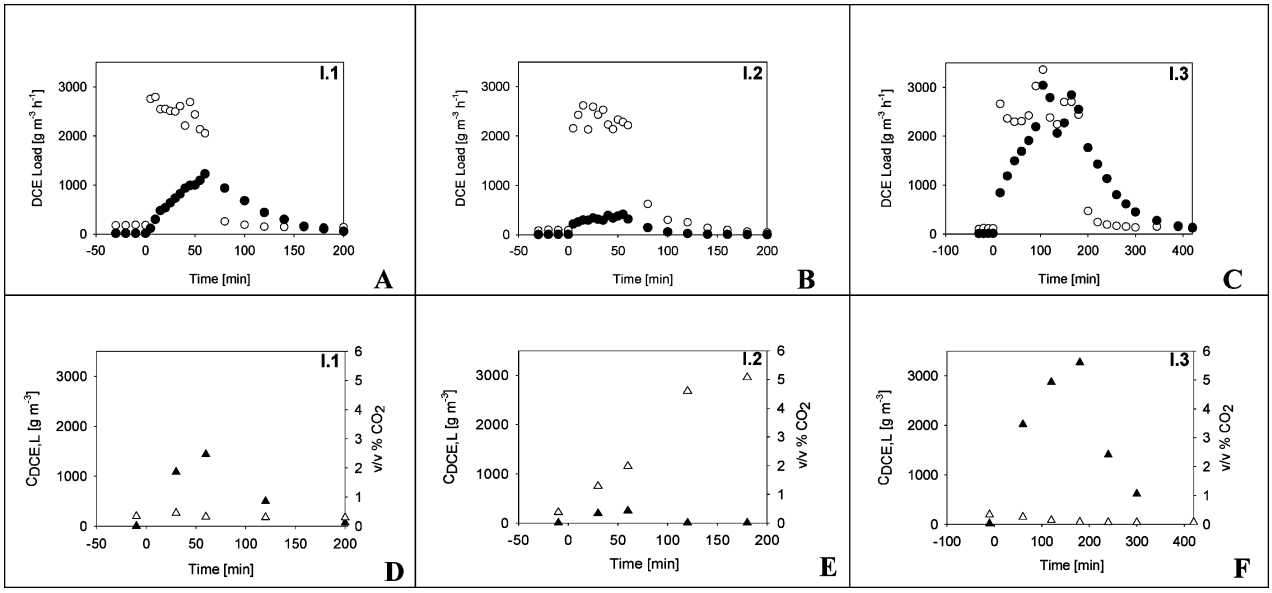

FIGURE 3. Evolution of DCE inlet loads, outlet loads, biomedium DCE concentration ($C_{DCE,L}$), and outlet carbon dioxide (% v/v) during the DCE pulses applied to system I. Figures are given as loadings per $m^3_{bioscrubber}$. System I, BO: A, D. pulse I.1 (1 h); B, E. pulse I.2 (1 h); C, F. pulse I.3 (3 h); ○ bioscrubber DCE inlet load, experimental; ● bioscrubber DCE outlet load, experimental; ▲ biomedium DCE concentration ($C_{DCE,L}$); △ outlet carbon dioxide % v/v.

significantly during the pulse (Figure 3D), suggesting incomplete DCE mineralization.

Pulse I.2. One day after the introduction of pulse I.1, the DCE percentage removal had recovered to levels higher than 90%, but due to the shock load, the conditions were different. It was observed that before pulse I.1 the cells were mainly growing as a biofilm on the walls of the bioscrubber with 135 g m^{-3} suspended biomass concentration and after pulse I.1 the biofilm progressively detached and the suspended biomass concentration increased to 2634 g m^{-3} 4 days later. With this increased suspended biomass concentration, a second 1 h pulse was fed to the bioscrubber, by increasing the inlet DCE load from an average value of 91 to 2339 g m^{-3} h^{-1} and then decreasing to an average of 216 g m^{-3} h^{-1} (Figure 3B). The inlet DCE concentration increased from 8 to 195 g m^{-3} for 1 h and then decreased to 18 g m^{-3}. The biomedium DCE concentration did not reach inhibitory levels this time, increasing from 2 g m^{-3} before the pulse to 247 g m^{-3} after the pulse (Figure 3E). TOC also increased, but to lower levels than in pulse I.1 and carbon dioxide concentration increased from 0.37% before the pulse to 5.07% 2 h after the pulse (Figure 3E), indicating that there was a significant increase in the organic material metabolized by GJ10. The TOD_{DCE} was 456 g $m^{-3}_{bioscrubber}$ during pulse I.2 (Figure 5). Although the increase of the inlet DCE concentration was similar to that observed in pulse I.1, the response of the system was better, due to the higher suspended biomass concentration, and the effect of the pulse was diminished. The system recovered 2 h after the pulse, and a high DCE percentage removal was re-established.

Pulse I.3. The bioscrubber was challenged with a longer DCE shock load in pulse I.3. The inlet DCE load increased from 113 to 2575 g m^{-3} h^{-1} for 3 h, and then decreased to 201 g m^{-3} h^{-1} (Figure 3C). This corresponds to a change in the inlet DCE concentration from 9 to 215 g m^{-3} and then to 17 g m^{-3}. Intensive foaming of the biomedium was observed 1 h after the introduction of the pulse, suggesting that the microbial culture was under stress. The biomedium DCE concentration increased sharply from 14 g m^{-3} before the pulse to 3270 g m^{-3} after the pulse (Figure 3F), which resulted in 9125 g_{DCE} $m^{-3}_{bioscrubber}$ discharged (Figure 5). TOC concentration followed the same trend as that of DCE and, similar to the results of pulse I.1, was 40% higher than the expected TOC. Additionally, the carbon dioxide concentration decreased from 0.34% v/v to 0.07% v/v and remained at that level for the next few days of operation, indicating that the biological process had ceased to function (Figure 3F). The system did not recover, and GJ10 was eventually washed out. Although the suspended biomass concentration remained relatively high after pulse I.3, FISH analysis showed a complete lack of specific staining 3 days after the pulse, which indicates that strain GJ10 was inhibited. Figures S-1A and S-1A′ (Supporting Information) display DAPI (S-1A) and GJ10 specific probe (S-1A′) staining of the same cells taken from the bioscrubber before pulse I.3. These images show that before the pulse there was a significant number of GJ10 cells (S-1A′) growing in the community of the suspended culture (S-1A), while 3 days after the pulse GJ10 had almost completely disappeared from the bioscrubber (Supporting Information, S-1B and S-1B′).

The results presented above indicate that sharp increases of the DCE inlet load can cause accumulation of DCE to inhibitory concentration levels in the biomedium, high TOD_{DCE} values, nonrepeatable system behavior, system instability, or even complete failure of the biotreatment process. These observations are in general agreement with previous studies (*1*−*7*). As already discussed, a sunflower oil absorber placed prior to the bioscrubber should offer a very attractive solution to the problem.

3. System II: Oil-Absorber−Bioscrubber (OAB). The sunflower oil absorber was placed prior to the bioscrubber in order to control the DCE shock loads (Figure 1). As for system I, all the shock loads described below were introduced when the bioscrubber was operating at steady state and the DCE percentage removal was higher than 90%.

Pulse II.1. A 0.5 L portion of sunflower oil was loaded into the absorber, which was operated at 30 °C. The DCE inlet loading to the OAB was increased from 170 to 2096 g m^{-3} h^{-1} for 1 h and then decreased to 459 g m^{-3} h^{-1} (Figure 4A), corresponding to an increase of the inlet gas DCE concentration from 14 to 175 g m^{-3} that was eventually decreased to 38 g m^{-3}. The introduction of pulse II.1 to the absorber resulted in an increase of the inlet loading to the bioscrubber from 133 g m^{-3} h^{-1} before the pulse to 180 g m^{-3}

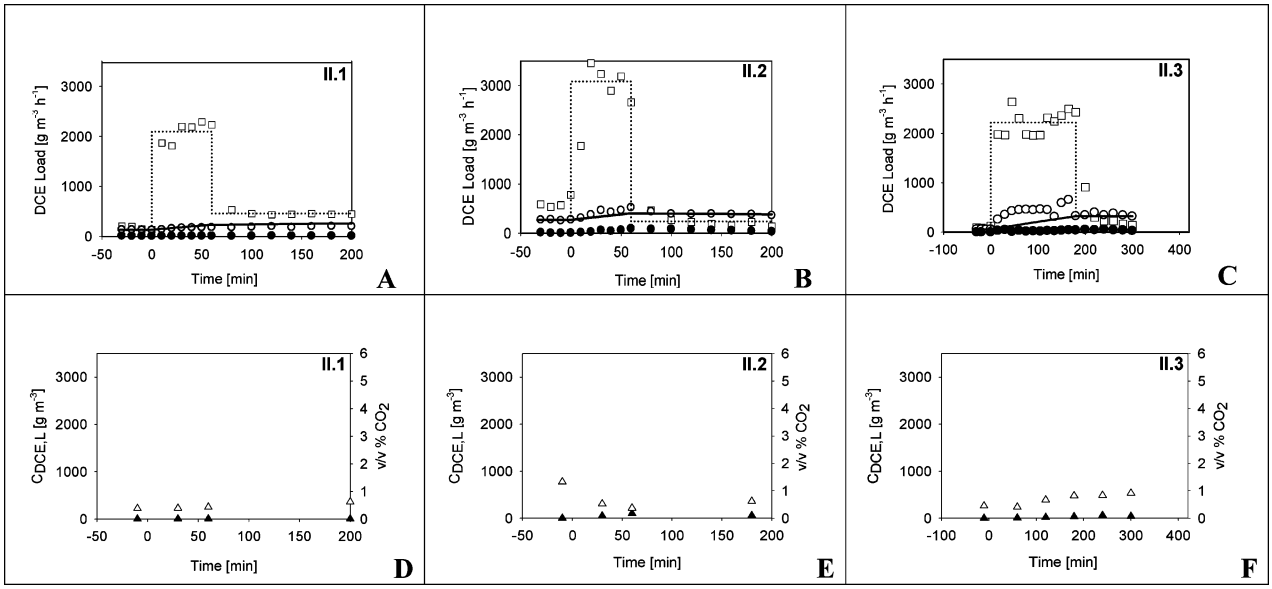

FIGURE 4. Evolution of DCE inlet loads, outlet loads, biomedium DCE concentration ($C_{DCE,L}$), and outlet carbon dioxide (% v/v) during the DCE pulses applied to system II. System II, OAB: A, D. pulse II.1 (1 h); B, E. pulse II.2 (1 h); C, F. pulse II.3 (3 h); □ absorber DCE inlet load, experimental; ○ bioscrubber DCE inlet load, experimental; ● bioscrubber DCE outlet load, experimental; (−) bioscrubber DCE inlet load, predicted; (···) absorber DCE inlet load, imposed; ▲ biomedium DCE concentration ($C_{DCE,L}$); △ outlet carbon dioxide % v/v.

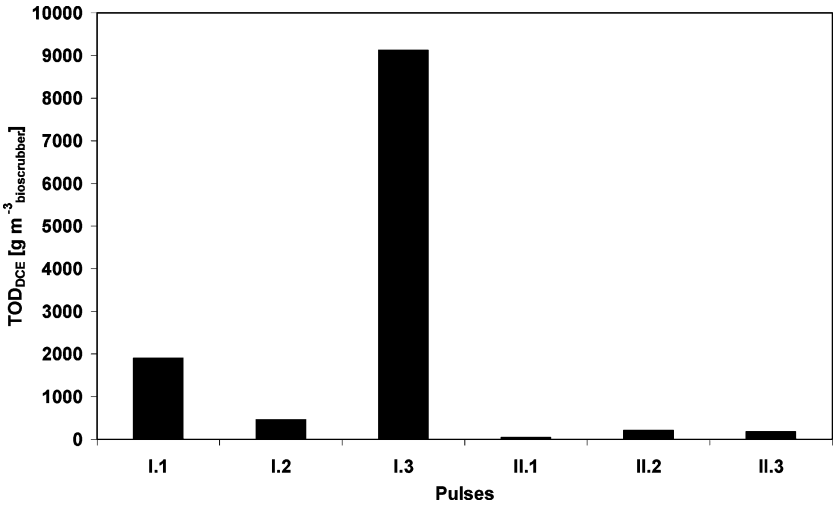

FIGURE 5. Total mass of DCE discharged from systems I (BO) and II (OAB) when exposed to pulses I.1−I.3 and II.1−II.3: system I, experiments I.1−I.3; system II, experiments II.1−II.3. The mass of DCE discharged was calculated by integrating the effluent DCE concentrations multiplied by flow rate of the gas and biomedium outlets from the bioscrubber and normalized by the bioscrubber volume. The integration was performed starting at the introduction of the pulse (time 0) and finishing at the end of the monitoring of each individual experiment (as displayed in Figures 3−4).

h^{-1} during the pulse. According to the modeling results, the inlet DCE load to the bioscrubber should increase by 76%, while the increase monitored experimentally was 35%. Nevertheless, the DCE shock load fed to the system was mainly absorbed into the oil during the pulse. After the end of the shock load, DCE slowly desorbed from the oil and was fed to the bioscrubber at noninhibitory loads for the following days of operation. Throughout the experiment, parameters such as biomedium DCE (Figure 4D) and TOC concentrations remained unchanged (7−9 and 0 g m^{-3} respectively). An increase of the carbon dioxide concentration was observed from 0.39 to 0.63% v/v, indicating an increase of the amount of organic carbon mineralized (Figure 4D). TOD_{DCE} was 38 g $m^{-3}_{bioscrubber}$ (Figure 5), which was significantly lower than the DCE discharged when the absorber was not present (pulse I.1: 1897 g $m^{-3}_{bioscrubber}$, pulse I.2: 456 g $m^{-3}_{bioscrubber}$).

Pulse II.2. Due to the dampening effect of the absorber for pulse II.1, the operating conditions of the bioscrubber did not change before pulse II.2 and biofilm detachment was not observed. For the DCE loading profile presented in Figure 4B, 0.55 L sunflower oil was used in the absorber and the performance of the system followed a similar trend to pulse II.1. Despite the fluctuations at the process inlet, the performance of the system was stable, leading to low increase of the bioscrubber DCE inlet load and low levels of TOD_{DCE} (206 g $m^{-3}_{bioscrubber}$, Figure 5). A third 1 h DCE pulse introduced to the OAB (data not shown) followed the same trend as in pulses II.1−II.2, indicating that the configuration which includes the absorber can give reproducible results over the introduction of sequential shock loads. In contrast, the configuration without the absorber had a different performance for two sequential 1 h DCE shock loads, due to biofilm detachment. Overall, a comparison between the two configurations in terms of the operational parameters' stability, such as DCE inlet loading to the bioscrubber, biomedium DCE and TOC concentrations, carbon dioxide, and TOD_{DCE},

undeniably shows the major advantage of the OAB option.

Pulse II.3. The OAB configuration was finally challenged with a 3 h DCE pulse in order to test the performance of the system under conditions that caused complete failure of the BO system. The absorber was loaded with 0.6 L of sunflower oil and the inlet DCE loading to the system was increased from an average value of 93 to 2219 g m^{-3} h^{-1} for 3 h and then decreased to 327 g m^{-3} h^{-1} (Figure 4C). The inlet gas DCE concentration increased from 8 to 185 g m^{-3} for 3 h and then decreased to 27 g m^{-3}. Due to the 3 h pulse, the DCE inlet load to the bioscrubber increased from an average value of 56 g m^{-3} h^{-1} to a maximum of 656 g m^{-3} h^{-1}. The total amount of DCE supplied to the system from the introduction of the shock load and up to the end of the experiment was 7311 g $m^{-3}_{bioscrubber}$, with more than 5000 g $m^{-3}_{bioscrubber}$ being absorbed into the oil. The absorbed DCE was desorbed and treated in the bioscrubber over the subsequent days of operation. The TOD_{DCE} was 173 g $m^{-3}_{bioscrubber}$, dramatically lower than the 9125 g $m^{-3}_{bioscrubber}$ discharged when the absorber was not present (Figure 5). The biomedium DCE and TOC concentrations increased slightly but remained at low levels (Figure 4F). The carbon dioxide produced also increased, indicating that the system was metabolizing the excess of DCE fed to the bioscrubber (Figure 4F). Despite the slight deterioration in the removal efficiency, the OAB system successfully dampened a 3 h shock load of the inhibitory compound, while under similar conditions the bioscrubber failed to control the DCE discharged when the absorber was not present.

The stability of system II was also confirmed throughout the culture by FISH analysis. There was no significant difference observed in the percentage of GJ10 cells present in the microbial population before and after the 3 h pulse for system II, in marked contrast to system I (Supporting Information, Figure S-1; C−C′, D−D′). Furthermore, "live−dead" cells analysis results indicate that,for system I, there was a significant increase of the inactive cells in the bioscrubber after the pulses (Figure 6A,B). In contrast, the increase of inactive cells in system II was lower, verifying the stability that the absorber provided to the system. Finally, we observed that the model prediction for the bioscrubber inlet load for the 3 h pulse (II.3) was not very accurate. This can be attributed to the rather simplified model used, which does not hold for longer and higher pulses. To scale-up the process, a more careful calculation and design of the parameters of the absorber may be required. However, these results point persuasively toward the effectiveness and potential of the hybrid OAB process.

4. Advantages of the OAB System. The proposed combined OAB system has several advantages over the previously studied systems:

(i) The absorber utilizes organic solvents or oils which are expected to have higher capacities than polymers (*17*, *18*) for most organic substrates.

(ii) Weber and Hartmans (*15*) studied the adsorption and desorption profiles of toluene in GAC, showing that GAC can exhibit high adsorption capacity for toluene (e.g., ∼0.3 g_{tol} g_{GAC}^{-1} adsorbed for 1 g_{tol} m^{-3} gas-phase concentration at 30 °C).

However, it is suggested that the efficiency of GAC in biological systems to dampen fluctuating inlet concentrations of inhibitory compounds can be severely affected by high moisture contents of the influent gas, reducing adsorption of pollutant and leading to low degradation rates (*15*). On the other hand, Peeva et al. (*32*) showed that the volumetric mass transfer coefficient of gas-phase decane to water−silicone−oil emulsions is independent of the emulsion composition. Therefore, humidity in the inlet gas does not have the same negative effect on dampening capacity for the

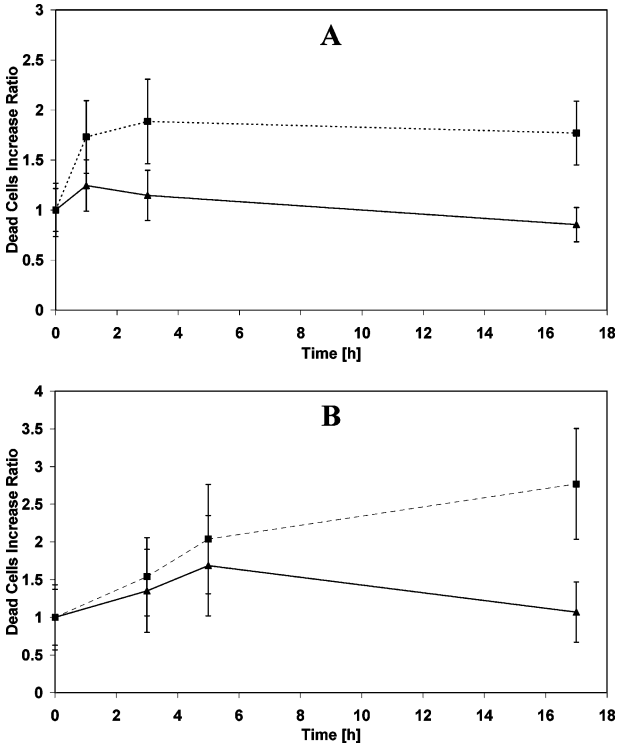

FIGURE 6. Increase of dead cells A, 1 h pulses (I.1, II.1); B, 3 h pulses (I.3, II.3); ■ dead cells increase ratio for system I (pulses I.1, I.3); ▲ dead cells increase ratio for system II (pulses II.1, II.3) in the bacterial population of systems I and II during and after the DCE pulses: Dead cells increase ratio = (percentage of dead cells at time *x*)/(percentage of dead cells at time 0) where time 0 indicates the beginning of the pulse. Percentage of dead cells = 100 × (number of cells stained with PI)/(number of cells stained with DAPI). The results are obtained as an average from 12 individual measurements at each point and the error bars are calculated for a confidence interval of 95%.

oil absorber system, although, in some extreme cases, it might affect the oil recirculation. Additionally, heating and cooling GAC to influence adsorption and desorption is not as easy with GAC as it is with sunflower oil. Also, in case the absorbent or the adsorbent have to be discharged periodically, the pollutant retained in the column has to be treated in the bioreactor by passing a noncontaminated air stream through it to remove the pollutant. Weber and Hartmans (*15*) reported that the desorption of the pollutant from GAC is a difficult process, but such a problem was not monitored for the OAB system. Also, if a pollutant with different physical or chemical properties than DCE is fed to the process, sunflower oil could, if necessary, be replaced by a different absorber liquid. However, the selection of the absorbent should be carefully considered, taking into account the criteria mentioned previously.

(iii) The only constraint for the absorbent fluid choice in the OAB system is a low-volatility fluid, whereas TPPB systems are further restricted by biocompatibility, nonbiodegradability, and acceptable phase separation. Thus, the option for use of more cost-effective solvents in TPPB systems is often excluded during the solvent screening process. Although biodegradable solvents have been successfully applied in TPPBs through a combination of genetic modification and solvent selection (*33*−*35*), these steps are avoided for the OAB by keeping the solvent and the biomedium separated.

(iv) Finally, the sunflower oil is a very attractive absorbent, as compared to silicone oil (*7*), due to its high partition coefficient for DCE, low toxicity, and very low cost.

Nomenclature

$C_{G,DCE}$	gas-phase DCE concentration in equilibrium with oil DCE concentration [g m^{-3}]
$C_{G,in}$	DCE concentration in the bulk of the gas inlet of the absorber [g m^{-3}]
$C_{G,out}$	DCE concentration in the bulk of the gas outlet of the absorber [g m^{-3}]
$C_{i,oil}$	DCE concentration in oil i [g m^{-3}]
$C_{sun,oil}$	DCE concentration in sunflower oil [g m^{-3}]
G	total gas flow rate [m^3 s^{-1}]
K_La_{oil}	volumetric mass transfer coefficient in the absorber [s^{-1}]
$P_{i,oil}$	partition coefficient for DCE between oil i and air [-]
$P_{sun,oil}$	partition coefficient for DCE between sunflower oil and air [-]
T	absorber temperature [°C]
t	time [s]
V_{oil}	volume of sunflower oil [m^3]

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Supporting Information Available

The Supporting Information available for this work includes detailed description of the experimental setup, analytical methods, experimental procedures used for FISH and "live−dead" cells analysis. The Supporting Information also includes the mathematical model used for the description of the absorber, Table S-1 displaying the DCE partition coefficient and cost for different potential absorber oils, and Figure S-1 containing FISH analysis images of the bacterial cells during pulses I.3 and II.3. This material is available free of charge via the Internet at http://pubs.acs.org.

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