Biofiltration of TCE vapours in a mixed compost-inert carrier trickle bed

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Trichloroethylene (TCE) is a common air pollutant particularly stiff to be biodegraded. TCE removal has been here exploited using a pilot-scale biotrickling filter in counter-current conditions filled with a mixed compost-inert carrier bed. Bioreactor operated for about five months obtaining a maximum elimination capacity of about 5.6 g/(m^3h) and a removal efficiency between 50 and 85%. Pressure drop and pH inside the bed remained constant and did not affect bioreactor performance during the whole experiment. Using both organic and inert carrier likely reduced the compaction of the bed and limited the pH drop inside the reactor. Data of elimination capacity were fitted using an original Ottengraf-modified model for steady state conditions.

1. Introduction

Biotechniques for air pollution control have excited an increasing interest in the last years. The reason can be found in the fact that biotreatments have shown many advantages comparing with other control techniques: they operate at room temperature, are safe and effective, do not generate hazardous by-products, they require low investment and running costs. Many different air pollutants have been treated in bioreactors, including *Volatile Organic Compounds* (VOCs), NH_3 and H_2S. Trichloroethylene (TCE) is a very common and hazardous VOC, which is particularly stiff to be biodegraded. Besides being slowly soluble in water, its degradation pathway requires a cometabolite and it generates both toxic and acidifying compounds (Wilson and Wilson, 1984, Cox et al., 1998, Devinny et al., 1999). Conventional biofilters (BFs) and biotrickling filters (BTFs) are very common bioreactors for air pollution control which have been widely used for the removal of TCE as well (Sun and Wood, 1997, Lackey et al., 2002, Den et al., 2004, Iranpour et al., 2005). In both designs, degradation occurs by means of the passage of the contaminated gas throughout a packed bed covered with an active biofilm. Differences basically concern the system to supply water for maintaining biomass activity: while in BTFs a mobile liquid phase trickles throughout the bed and it is normally recirculated at the top of the bioreactor, in BFs design the right moisture level is mostly assured by a pre-humidification system. Trickling liquid is a good mean to supply alkali for pH control, or additional nutrients for biomass activity. Since the mobile liquid phase allows the control of the process, BTFs are often preferred. Organic packages are widely used in conventional biofilters, because of their high specific surface area, their good buffer properties, and because they already hold a well-developed biomass; on the contrary, organic packages are normally avoided in biotrickling filters, since the risk of bed compaction is much

higher. Inert carrier has conversely good mechanical properties but low buffer and retention capacity, and a biomass inoculum is required. Biotrickling filters can operate both in co-current and in counter-current mode, and no experimental evidence has demonstrated which is the optimal design configuration (Kennes and Veiga, 2001). Counter-current operation is normally avoided, because process performance could be affected by the great amount of pollutant sorbed and recirculated with the leachate at the top of the reactor.
In this study, the performance of a biotrickling filter treating TCE was evaluated. BTF design was preferred because of the possibility to remove toxics from inside the bed, to control the pH of the leachate and to add the required primary substrate for the cometabolic degradation. Packed bed was constituted by a mixture of organic and inert carrier, in order to have good mechanical properties and high buffer and retentive capacities as well. BTF operated in counter-current mode to promote mass transfer. Before being recirculated, the leachate was treated in an additional trickle bed unit set below the gas inlet, in order to reduce the content of pollutant into the liquid phase: with this design, the limits of counter-current application were overcome.
Experimental data of elimination capacity and mass loading rate were fitted using a new mathematical model, whose theoretical bases were drawn from Ottengraf's study (Ottengraf and van den Oever, 1983). The model here proposed is based on one equation only and it can simultaneously take into account effects of reaction and diffusion limitations on the overall process rate.

2. Materials and methods

2.1 Pilot-plant

The BTF under investigation was configured as a two glass cylinders unit (see figure (1)). Each cylinder was 1 meter high, with an internal diameter of 9.5 cm and it was filled with a packed bed of 6 l volume. Counter-current mode was achieved in each cylinder using an upward gas flow. Gas stream was generated by a membrane pump and it was divided into three streams. The main stream had an average flow rate of 210 l/h: it passed throughout two gas bubbling bottles for pollutant addition and it was subsequently fed at the bottom of the upper cylinder. A lower gas stream flew throughout the lower cylinder for maintaining biomass activity. Outlet gas stream had a gas flow rate of 280 ± 5 l/h. Third stream served as split-flow, to avoid stress on the air pump. A peristaltic pump recirculated the trickling liquid and the nutrients solution at the top of the bioreactor. Trickling liquid flow rate was maintained constant at 4.50 ± 0.2 ml/min.

2.2 Packing

Packing was constituted by a mixture of compost and little glass hollow cylinders with a organic/inert volume ratio of 1:5. Compost came from a composting plant treating municipal solid wastes: it had an overall density of 510 kg/m^3 and a humidity of 30%. Glass cylinders were 1 cm height with an external diameter of 1 cm, 2000 kg/m^3 of bulk density and a specific surface area of about 250 m^2/m^3.

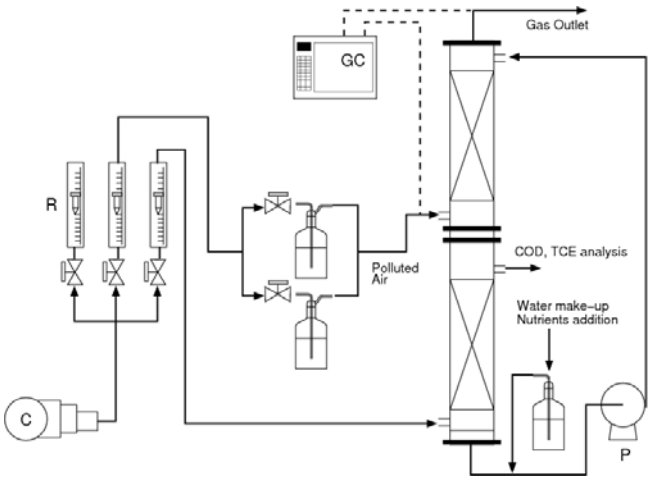

Figure 1. Scheme of the pilot-scale BTF under investigation. C: air pump, P: recirculating pump, R: rotameters.

2.3 Analysis

TCE concentrations in the gas and in the trickling liquid were measured by means of a Gas Chromatograph (DANI GC1000 DPC) equipped with an *Electron Capture Detector* (ECD). Gaseous samples were collected and automatically injected by an autosampler provided with a sampling loop of 250 µl. According with the standard methods for solvent determination in aqueous samples, *static head space* method was employed to measure TCE concentration in the leachate. The pH of the liquid phase was measured using a HANNA HI98150 portable pH-meter. The pressure drop along the whole bioreactor was also considered and it was measured by means of an U-shaped manometer. The measurement of the gas flow rate was achieved by some rotameters and by a volumetric flowmeter (SIM Brunt).

2.4 Nutrients solution

A simple nutrients solution was prepared with Sodium Acetate (20 g/l) and Sodium Nitrate (10 g/l). Nutrients addition was set in order to obtain a recirculated liquid with 120 mgCOD/l and 11 mgN-NO_3/l. Further nutrients were supposed to be provided by the compost itself.

2.5 Biotrickling-filter piloting

The study was carried out for about 5 months. First month was necessary to assess the fluidodynamic stability of the bioreactor in absence of pollutants. Afterwards, a very diluted waste gas containing TCE was fed to the system during a period of about 2 months, for biomass acclimatization. The first day of TCE addition was set as "day zero". After that, TCE concentration in the inlet gas flow was increased until a maximum value of 0.192 g/m^3, in order to determine the maximum degradation capability of the pilot-plant.

3. Theoretical model

The model here proposed is a mathematical modification of the Ottengraf and van den Oever model (Ottengraf and van den Oever, 1983). The original model is based on

some simple assumptions: stationary state, zero-order kinetics for biological degradation, Henry's law for fluid interface equilibrium, two phases (gas and water/biofilm), one pollutant only, and plug flow conditions. Depending on the profile of pollutant concentration into the water/biofilm phase, two different regimes could be identified. When inlet gas stream is highly contaminated, pollutant can be easily absorbed into the water/biomass film and it diffuses completely throughout it. In such condition, biomass could not be able to degrade all the amount of pollutant sorbed, and biological reaction is the rate determining step of the process. Conversely, with a diluted gas flow, mass transfer is moderate and it determines the rate of the process. By the mass balances for the gas phase and the water/biofilm phase, two equations can be written for the reaction limitation region (1) and for the diffusion limitation region (2) respectively:

$$\frac{C_{go}}{C_{gi}} = 1 - \frac{A_s k_0 \delta H}{C_{gi} U_g} \tag{1}$$

$$\frac{C_{go}}{C_{gi}} = \left(1 - \frac{A_s H}{U_g} \sqrt{\frac{k_0 D}{2 C_{gi} m}} \right)^2 \tag{2}$$

where C_{go} and C_{gi} are the pollutant concentration in the outlet and in the inlet gas stream respectively [g/m^3], A_s is the specific surface area [m^2/m^3], k_0 is the zero-order kinetic constant [g/(m^{3}h)], δ is the biofilm thickness [m], D is the diffusivity in water [m^2/h], m is the air/water partition coefficient [g/g], H is the bed height [m], and U_g the superficial gas velocity [m/h]. By using the definition of elimination capacity (EC, [g/(m^{3}h)]) and mass loading rate (L, [g/(m^{3}h)]), equation (1) and (2) can be rewritten in terms of these new process parameters (Delhomènie et al., 2002):

$$EC_{rl} = A_s k_0 \delta \; ; \tag{3}$$

$$EC_{dl} = L \left(1 - \left(1 - A_s \sqrt{\frac{k_0 D}{2m}} \sqrt{\frac{V}{QL}} \right)^2 \right) \tag{4}$$

with V the bed volume [m^3] and Q the volumetric gas flow rate [m^3/h]; the subscript *rl* stands for reaction limitation and the subscript *dl* stands for diffusion limitation. A simple equation can be used to pass continuously from equation (3) to equation (4). This equation should consider that, as the inlet concentration increases, the contribution of mass transfer limitation will reduce, while the contribution of the biological reaction will become greater. The following equation can accomplish these conditions:

$$EC = EC_{rl} + \frac{EC_{dl} - EC_{rl}}{1 + \left(L / L_{cr} \right)^p} \tag{5}$$

where L_{cr} is the mass loading rate at which transition between reaction and diffusion limitation area occurs [g/(m^{3}h)] and p is a dimensionless parameter of the model. Using the critical Thiele number as proposed by Ottengraf, L_{cr} can be calculated as follows:

$$L_{cr} = \frac{\delta^2 k_0 m Q}{2DV} \quad (6)$$

Equation (5) was used to fit the data of elimination capacity and mass loading rate obtained by the experiments.

4. Results and Discussion

TCE concentrations in the inlet and in the outlet gas flows are reported in figure (2) with the corresponding removal efficiency. It can be observed that the total TCE removal was not achieved even at very low inlet concentrations: this fact was likely due to some mass transfer limitations or to an incomplete biomass acclimatization. From day 30 to day 90, the removal efficiency remained mainly constant, with values included between 70% and 80%. In the following days, the progressive increase in TCE concentration reduced the process efficiency to a minimum value of about 50%. At the maximum inlet concentration of 0.192 g/m^3, a removal efficiency of 63.4 % was obtained. Considering the TCE emissions limit of 0.02 g/m^3, as established by the Italian legislation (D. Lgs 152/2006), outlet stream exceeded this limit for inlet concentrations higher than 0.07 g/m^3.

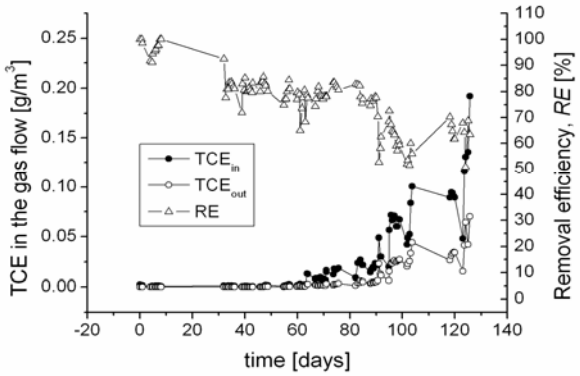

Figure 2. TCE concentration in the inflow and in the outflow and the corresponding removal efficiency during the whole experiment along.

Figure (3) reports data of TCE concentration into the leachate sampled at the top and at the bottom of the lower unit. Obviously, TCE_{top} increased as the pollutant concentration in the gas inflow increased. The removal efficiency related to the leachate (RE_L) was higher than 95% during the whole experiment. Stripping effects and biological activity could both contribute to this high removal. Thanks to the lower unit, the amount of TCE recirculated at the top of the BTF was therefore strongly reduced, limiting the problems related to counter-current operations. However, since the ratio between gas and liquid flow rates was very low, the favourable contribute of the leachate treatment to the overall removal efficiency was almost negligible. Lower unit can play a more important role when operating with low gas and high trickling liquid flow rates or with more soluble pollutants.

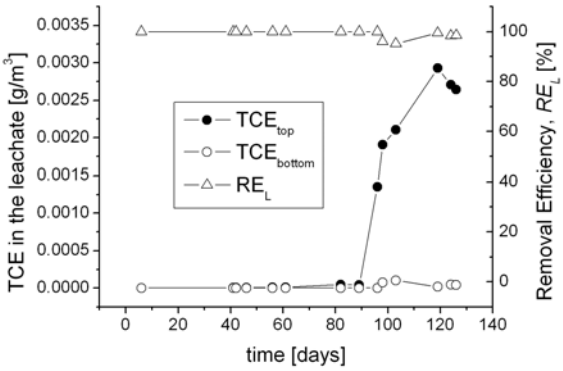

Figure 3. TCE concentration in the leachate at the top and at the bottom of the lower unit and the corresponding removal efficiency.

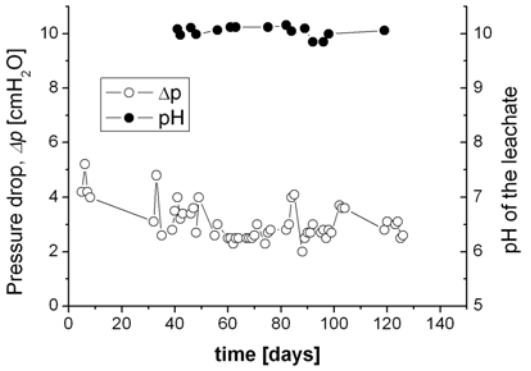

Figure 4. Pressure drop along the whole bioreactor and pH of the leachate during the whole experiment.

As it can be observed in figure (4), pressure drop and pH of the leachate remained mainly constant during the experiment. This fact can be attributable to the employment of a mixture organic/inert carrier as packed bed. An average pressure drop of 3.1 cmH_2O was obtained and the moderate fluctuations in its values were essentially due to tube fouling rather than to an effective pressure drop inside the bioreactor. Leachate had a constant pH with an average value of 10.02. Alkaline conditions are not common in biofiltration processes (Kennes and Veiga, 2001), since it has been reported that biomass activity is promoted at pH values close to 7, for TCE removal as well (Misra and Gupta, 2001). Buffer capacity of compost reduced the acidifying effect of some by-products of TCE biodegradation. Since its alkaline properties, sodium acetate could also have given its contribution to pH control.

Figure (5) reports data of elimination capacity (*EC*) vs. mass loading rate (*L*). An *EC* maximum value of 5.61 g/(m^3h) was obtained for L = 8.86 g/(m^3h). This value was much higher than that reported by other studies concerning TCE removal in conventional biofilters and biotrickling filters (Sun and Wood, 1997, Lackey et al., 2002, Den et al., 2004, Jung and Park, 2005). This fact confirms the goodness of the process for the removal of this target pollutant. By the same graph, it can be observed

that the condition of reaction limitation area was not achieved along the whole experimental range. Indeed, when this condition occurs, elimination capacity is constant and it does not depend on the mass loading rate. Thus, it can be stated that mass transfer had limited the process rate during the whole experiment.

Figure (5) reports also the curve obtained by data fitting using the Ottengraf's modified model. Parameters used in the model are reported in table (1). Data fitting was carried out using the Levenberg-Marquardt algorithm, obtaining a coefficient of determination R^2 of 0.921. Considering the theoretical basis of the new Ottengraf's modified model, data from both reaction and diffusion limitation area should be available to improve the goodness of the model itself. In this case, the lack of experimental data for the reaction limitation condition had a particular effect on the determination of the biofilm thickness, which appears in the definition of EC_{rl} only. Indeed, the value of this parameter obtained by data fitting was extremely high (about 1.6 cm), with no physical meaning, considering the experimental set-up. In spite of this, the model could be an useful mean for a first evaluation of the process and for the determination of a good initial set of parameters for a further numerical implementation.

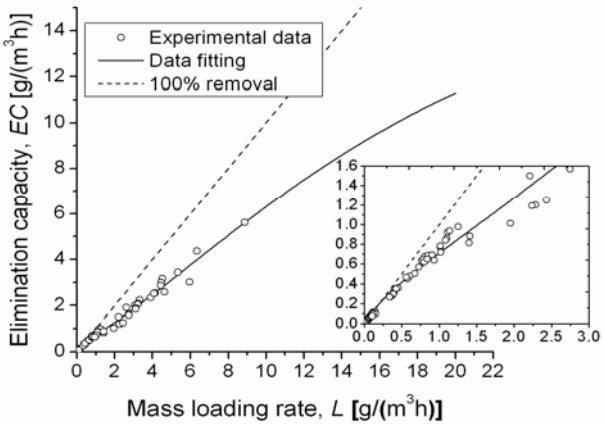

Figure 5. EC vs. L plot and curve obtained bt data fitting, using the Ottengraf's modified model

Table 1. List of fixed and fitted parameters used in the Ottengraf's modified model. References: (a) Folsom et al., 1990, (b) Chiao et al., 1994

Fixed parameters	Values	Fitted parameters	Initial Set	Final Set
Average gas flow rate Q [m^3/h]	0.2816	Specific surface area A_s [m^2/m^3]	1000	999.496
Bed volume V [m^3]	0.006	Biofilm thickness δ [m]	0.001	0.01614
Air/water partition coefficient m [g/g]	0.4 (a)	Zero-order kinetic constant k_0 [g/(m^3h)]	10	1.21367
Diffusivity in water D [m^2/h]	3.75×10^{-3} (b)	Critical mass loading rate L_{cr} [g/(m^3h)]	25.03	19.9813
		Exponent, p	1	1.64868

5. Conclusions

The effectiveness of a bioreactor, characterized by a mix organic/inert trickle bed was here demonstrated for the treatment of TCE vapours. The choice of this specific packing allowed to carry out long-term operation: indeed, the typical malfunctioning of this kind of process (high pressure drop and bed acidification) had not been observed during the whole experiment. The biotrickling filter under investigation had shown good efficiency and high elimination capacity. However, its effectiveness could be strongly enhanced, reducing limitations due to mass transfer, which had been demonstrated to be the rate determining step of the process. The lower trickle-bed unit could remove almost completely the pollutant content of the leachate. Anyway, its contribution to the overall removal efficiency can be enhanced if operating with higher trickling liquid flow rates. This oppurtunity is currently under investigation and it is one of the most promising features for this bioreactor design. A new simple model was proposed and validated. The model shows the advantage of having one equation only which can be applied for the entire range of mass loading rate.

6. References

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