Biofiltration of industrial waste gases in trickle-bed bioreactors

Case study: trichloroethylene removal

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31 Gennaio 2008
A Giuly...
Air pollution is an alarming problem for the future of our planet. Because the increasing world-wide industrialization, the development of economic and effective techniques to control air emissions is necessary.

Among the most important and hazardous atmospheric pollutants, the Volatile Organic Compounds (VOCs) have been intensively investigated. That is because they are responsible of photochemical smog in the troposphere, they can contribute to reduce the ozone layers and because they are hazardous compounds for human beings and the overall biosphere.

Biotechniques to control air pollution have been of greater and greater interest in the last years. Initially developed for the treatment of odours from composting and waste water treatment plants, such techniques have been successfully employed also for VOC control and biogas desulfurization.

Comparing with other control techniques, biological oxidation has many advantages: it can operate with high flow rates and low pollutant concentrations, it operates at room temperature, it does not generate toxic or hazardous by-products, and, above all, it requires low investment an operating costs.

The capability of certain microorganisms to degrade gaseous pollutants has been exploited in many bioreactors, which mainly differ in the system employed to provide water for the life of the microorganisms.

The most used bioreactors are conventional biofilters and biotrickling filters. While in the latter a mobile liquid phase trickles throughout a packaging, in the conventional biofilters, the required moisture is granted by the pre-humidification of the inlet gas flow.

Trichloroethylene (TCE) is a chlorinated VOC and it is particularly stiff to be biodegraded: it is poorly soluble and scarcely biodegradable, it requires cometabolism and it generates toxic and acidifying by-products.

The present study concerns the development an the validation of an adequate strategy for the employment of biotechniques for the control of TCE emissions.

Initially, a literature study was required for individuating the problems and the limits concerning biotechniques and the degradation of the target pollutant. From this study, biotrickling filter was reckoned to be the most appropriate and affordable technology. A pilot-scale biotrickling filter was than realized with all the accessory equipments.

Reactor was filled with a mixture of compost and small glass cylinders for an overall bed volume of almost 6 liters. Compost was selected because it can provide a native and well-developed biomass, with high buffer and retention properties, high specif surface area \((0.7 \times 10^6 \text{ m}^2/\text{m}^3)\) and cheapness. Glass cylinders can give to the bed an higher mechanical strength,
reducing the risk of bed compaction, channeling and flooding. The employment of a mixture of organic/inert carrier is the first important remark for the present bioreactor.

The second remark is the introduction of a new biofilter unit below gas inlet for the treatment of the leachate. This particular configuration reduces the amount of TCE recirculated at the top of the reactor, increasing the efficiency of the counter-current operation.

TCE concentration in the gas and in the leachate flows, pressure drop, pH and COD of the leachate were daily monitored.

Bioreactor operated for longer than 6 months: an initial period was required to evaluate the optimal fluidodynamic regime and to assess biomass acclimatization to TCE.

TCE analyses confirmed the effective removal of pollutant, with efficiencies higher than 75% and elimination capacities of over than 5 g/(m$^3$·h).

During the whole operation, pH remained nearly constant and no abrupt increase of pressure drop was noticed.

Other experiments were carried out to evaluate the behaviour of the bioreactor under transient conditions and to evaluate the effects of gas and leachate flow rates on the removal efficiency.

The knowledge of interaction between biomass and pollutant is very important for biofilter design. Respirometric techniques have been widely used for the optimization of the control of wastewater treatment plants, to determine the growth and decay biomass kinetic and to fractionate the organic substrate of the influent. These techniques have been only recently applied to solid matrix, especially to assess compost stability. However, many useful hints can arise from respirometric approach to biofiltration.

A simple automatic equipment was realized for respirometric analysis, with integrated data-logging and control system. This new apparatus was employed to evaluate the role of TCE on the activity of native compost biomass.

Microbial activity is strongly reduced by the presence of TCE and, probably, of some inhibitory by-products. However, a partial recovery of the activity was observed during long-term test, likely due to a biomass acclimatization.

Moreover, in the present study, a new mathematical model was proposed and validated. The model was obtained starting from the Ottengraf and Van den Overs model (1983). It can take into account both effects due to diffusion and reaction limitations. The new model shows the advantage of an algebraical analytical solution and of a reliability in a wide range of mass inlet load.

Model was investigated with a sensitivity analysis and validated by fitting with the experimental data.
L’inquinamento atmosferico rappresenta ormai da anni un grasso problema per il futuro dell’uomo e del nostro pianeta. La crescente industrializzazione su scala mondiale ha reso ancora più necessario lo sviluppo di tecniche per il controllo delle emissioni gassose che siano economiche ed efficaci al contempo.

Tra i principali inquinanti atmosferici, i composti organici volatili (VOCs) sono stati oggetto di ampio studio. Essi sono tra i principali responsabili dello smog fotochimico nella troposfera e dell’assottigliamento dello strato di ozono, hanno effetti gravi sull’uomo anche per brevi tempi di contatto e vengono accumulati nei tessuti adiposi degli animali entrando nella catena alimentare.

Tra le tecniche di controllo delle emissioni di VOCs, un sempre maggiore interesse è stato riservato ai processi di ossidazione biologica o biofiltrazione. Nati inizialmente per la riduzione degli odori da centri di compostaggio o impianti per acque reflue, tali processi sono stati applicati con successo in altri campi, quali principalmente il controllo dei VOC e la desolforazione del biogas.

Rispetto alle altre tecniche di rimozione, la biofiltrazione presenta innumerevoli vantaggi: può operare con alti flussi a basse concentrazioni, lavora a temperatura ambiente, non genera sottoprodotti tossici e soprattutto richiede bassi costi di investimento e di gestione.

La capacità di certi microorganismi di degradare gli inquinanti presenti in un flusso gassoso è stata utilizzata in diversi tipi di reattori biologici, che differiscono essenzialmente nel modo di somministrazione dell’acqua. Infatti, al pari dei substrati carbonioso e nitrico, l’acqua è un elemento indispensabile per l’attività microbica.

I bioreattori più utilizzati sono i biofilteri e i biotrickling filters. Nei biofilter non si ha una fase liquida mobile e tutto l’apporto d’acqua viene garantito da un sistema di preumidificazione a monte del reattore stesso. Nei biotrickling filters, al contrario, è presente un liquido che attraversa tutta la lunghezza del reattore e che serve come sistema di controllo delle condizioni del processo.

Il processo di biofiltrazione è stato applicato con successo anche su diversi impianti a scala reale e per la rimozione di diversi tipi di contaminante gassoso, sia esso organico che inorganico.

Il tricloroetilene (TCE) è un VOC clorurato che presenta alcune proprietà che ne rendono difficile la rimozione biologica: presenta bassa solubilità in acqua e scarsa biodegradabilità, può venir degradato solo per via catabolica e genera sottoprodotti acidi o inibitori dell’attività microbica.

Il presente studio si propone di individuare una procedura per il controllo delle emissioni di TCE in atmosfera mediante biofiltrazione.
Inizialmente è stato affrontato un dettagliato studio della letteratura al fine di individuare le principali problematiche relative al processo e al tipo di inquinante. Da tale studio, si è scelto il *biotrickling filter* come bioreattore ideale per la rimozione del TCE. È stato quindi realizzato un impianto su scala pilota, operante come *biotrickling filter* ed equipaggiato con tutte le strumentazioni necessarie per il suo corretto funzionamento.

Il reattore è stato riempito con compost e piccoli cilindri di vetro, per un volume totale del letto di circa 6 litri. Il compost è stato scelto come riempimento per la capacità di fornire una biomassa complessa e attiva, per le sue proprietà di buffer e ritenzione idrica, per la sua bassa densità, la sua economicità e la sua elevata superficie specifica (0.7×10⁶ m²/m³). I cilindri di vetro, invece, conferiscono al letto migliori proprietà meccaniche e riducono il rischio di compattazione del riempimento, che rappresenta una delle principali cause di malfunzionamento per questi tipi di reattore.

Un altro aspetto importante dell'impianto realizzato è la presenza di una unità al fondo del *biotrickling filter* per il trattamento del percolato. La riduzione della quantità di contaminante presente nel liquido recircolato consente infatti l’ottimizzazione del processo operante in contro-corrente, migliorando il trasferimento di massa tra la fase gassosa e la fase liquida.

Questa unità presenta un letto dal volume e dalle caratteristiche identiche al letto del *biotrickling filter* precedentemente descritto e la biomassa viene mantenuta vi tale tramite un debole flusso ascendente d’aria.

Sono state prese in esame le portate di ingresso per le fasi gassose e liquide, la concentrazione di TCE all’ingresso e all’uscita del reattore nella fase gas e nel percolato, le perdite di carico lungo il reattore e le condizioni di pH e il COD del liquido di ricircolo.

Il reattore ha operato continuatamente per oltre 6 mesi, di cui i primi sono stati necessari per la valutazione del corretto regime fluidodinamico e per l’acclimatazione della biomassa con il contaminante.

Le analisi effettuate sull’impianto hanno dimostrato l’effettiva capacità della biomassa indigena del compost di degradare il TCE, con efficienze di rimozione medie superiori al 75% e con una *elimination capacity* massima di oltre 5 g/(m³·h).

Durante il periodo di funzionamento, non si sono riscontrati evidenti riduzioni del pH del percolato e nemmeno eccessivi incrementi della perdita di carico.

Sono state inoltre effettuate altre misure per valutare il comportamento dell’impianto in regime transitorio e per valutare l’effetto delle portate di gas e liquido sull’efficienza di rimozione.

Uno studio più dettagliato del processo richiede la conoscenza delle costanti cinetiche di degradazione dell’inquinante. Tali costanti sono utili per la realizzazione di un modello e quindi della previsione delle prestazioni di un determinato tipo di reattore a partire dalle condizioni operative.

La respirometria è una disciplina correntemente utilizzata nell’ambito del trattamento di reflui liquidi per la determinazione delle costanti biologiche. Tale disciplina è stata solo recentemente estesa alle matrici solide, in particolare per lo studio della stabilità biologica del compost. Nel campo della biofiltrazione è stata invece utilizzata per lo studio delle variazioni dell’attività microbica in operazioni di lunga durata.

È stato realizzato un sistema automatico per l’analisi respirometrica, con la possibilità di inserire i dati al *computer* e di evitare le regioni a bassa concentrazione di ossigeno che inficerrebbero la prova. Con tale apparato è stato possibile valutare l’effetto del tricloroetilene sulla biomassa nativa del compost.
Tale effetto si manifesta essenzialmente come una forte riduzione dell’attività microbica dovuta sia alla presenza del contaminante che, probabilmente, di alcuni sottoprodotti tossici o inibitori. L’effetto tossico del TCE si è ridotto di molto durante la sperimentazione, suggerendo una possibile acclimatazione della biomassa.

È stato inoltre proposto un originale modello matematico, a partire dagli studi di OTTEN-graf e Van den Oever (1983). Il nuovo modello si basa su una formulazione matematica che consente di passare con continuità dall’equazione valida in condizione di diffusione limitante a quella di reazione limitante. La soluzione che ne risulta presenta una forma analitica semplice ed ha validità su tutto il range di concentrazione di contaminante in ingresso.

Sui dati ottenuti dalla sperimentazione è stato effettuato il fitting ottenendo buona corrispondenza con i dati da modello. Il modello stesso è stato poi sottoposto ad analisi di sensibilità per verificare l’effetto dei parametri principali sull’efficienza di rimozione.
Nomenclature

Roman Letters

$A_s$ Specif surface area or specific interface area [$m^2/m^3$]

$C^*$ Pollutant concentration in the gas flow at which passage between reaction and diffusion limitation area occurs [$g/m^3$]

$C_{ads}$ Pollutant concentration onto a sorber [$g/g$]

$C_g$ Concentration of the pollutant in the gas flow [$g/m^3$]

$C_l$ Concentration of the pollutant in the liquid phase [$g/m^3$]

$C^*_l$ Saturation concentration for the pollutant in the liquid phase for the two-films theory [$g/m^3$], see equation (2.11), page 14

$C_{g,1}$ TCE concentration in the stream $G_1$ [$g/m^3$], page 67

$C_{g,2}$ TCE concentration in the stream $G_2$ before reaching the pilot-plant [$g/m^3$], page 67

$C^*_{g,2}$ TCE concentration in the gas flow at the top of the lower unit of the pilot-plant [$g/m^3$], page 67

$C_{g,in}$ Concentration of the pollutant in the gas phase in the inlet flow [$g/m^3$]

$C_{g,out}$ Concentration of the pollutant in the gas phase in the outlet flow [$g/m^3$]

$C_{l,in}$ TCE concentration in the leachate, at the top of the lower unit of the pilot-plant [$g/m^3$]

$C_{l,out}$ TCE concentration in the leachate, at the bottom of the lower unit of the pilot-plant [$g/m^3$]

$C_{max}$ Maximum adsorbed concentration for Langmuir’s isotherm [$g/g$], see equation (2.13), page 15

$EBRT$ Empty bed residence time [h], see equation (2.17), page 16

$EC$ Elimination capacity [$g/(m^3-h)$], see equation (2.16), page 16

$EC_{dl}$ Elimination capacity referred to diffusion limitation area [$g^3/(m^3-h)$]

$EC_{max}$ Maximum elimination capacity [$g/(m^3-h)$], page 17

$EC_{rl}$ Elimination capacity referred to reaction limitation area [$g^3/(m^3-h)$]

$G_1$ Volumetric waste gas flow rate with, at the middle of the pilot-plant [$m^3/h$], page 67
VIII

$G_2$  Volumetric waste gas flow rate with, passing throughout the lower unit in the pilot-plant [m$^3$/h], page 67

$H$  Height of the bioreactor bed [m]

$h$  Direction along the height of the bioreactor [m]

$H'$  Dimensionless Henry’s constant [-]

$IR$  Respirometric index for compost stability [mgO$_2$/(kgVSS-h)], see equation (10.10), page 93

$k_0$  Zero-order kinetic constant [g/(m$^3$·h)]

$k_1$  First-order kinetic constant, [h$^{-1}$]

$k_d$  Endogenous decay coefficient [h$^{-1}$], see equation (2.8), page 13

$K_{ads}$  Freundlich’s isotherm constant [m$^3$/g], see equation (2.14), page 15

$K_I$  Andrew’s inhibition constant [g/m$^3$], see equation (2.5), page 12

$K_{ads}$  Langmuir’s isotherm constant [g/m$^3$], see equation (2.13), page 15

$k_m$  Pollutant concentration in the (solid/water) phase on pollutant concentration in the gas phase for Devinny and Hodge model [], see equation (4.20), page 36

$K_S$  Monod’s half-velocity constant for the substrate S[g/m$^3$], see equation (2.2), page 11

$k_t$  Mass transfer coefficient for the two-films theory [h$^{-1}$], see equation (2.11), page 14

$K_{O_2}$  Monod’s half-velocity constant for Oxygen [gO$_2$/m$^3$], see equation (2.4), page 12

$K_{ow}$  Octanol/water partition coefficient [-]

$L$  Mass loading rate [g/(m$^3$·h)], see equation (2.15), page 16

$L^*$  Inlet load at which the passage between reaction and diffusion limitation area occurs [g$^3$/(m$^3$·h)], see equation (4.25), page 37

$L_C$  Critical mass loading rate [g/(m$^3$·h)], page 17

$m$  Air-water partition coefficient for the pollutant [-]

$N$  Mass flux of the pollutant from gas phase to the liquid phase[g/(m$^2$·h)]

$n$  Freundlich’s isotherm constant, see equation (2.14), page 15

$OUR$  Oxygen uptake rate [gO$_2$/(m$^3$·h)], see equation (10.6), page 90

$p$  Parameter of the Ottengraf-modified model [-], see equation (4.25), page 37

$Q_L$  Volumetric trickling water flow rate [m$^3$/h]

$Q_V$  Volumetric gas flow rate [m$^3$/h]

$r_d$  Endogenous decay rate [gVSS/h], see equation (2.8), page 13
**Greek Letters**

- $\delta$: Biofilm thickness [m]
- $\Delta p_{\text{max}}$: Maximum negative pressure revealed during stability assay [mbar], see equation (10.10), page 93
- $\eta$: Bioreactor efficiency [-]
- $\lambda$: Penetration of the pollutant into the biofilm or thickness of the active biofilm for diffusion limitation area [m], see equation (4.14), page 34
- $\mu$: Specific microbial growth rate [h$^{-1}$]
- $\mu_{\text{max}}$: Maximum specific growth rate [h$^{-1}$], see equation (2.2), page 11
- $\sigma$: Dimensionless coordinate perpendicular to gas-liquid interface [-], page 33
- $\theta$: Temperature depending coefficient for determining biomass activity [-], see equation (2.7)
- $\phi$: Dimensionless Thiele module [-], see equation (4.6), page 33
- $\phi_1$: Dimensionless Thiele module with first-order kinetic [-], see equation (4.19), page 34
- $\phi_{\text{cr}}$: Critical dimensionless Thiele module [-], see equation (4.11), page 33, page 12
- $\chi$: Molecular connectivity index [-]

**Special Characters**

- $D$: Diffusion coefficient for the pollutant into the liquid phase [m$^2$/h]
- $U_g$: Superficial gas velocity [m/h]
# Contents

## 1 Air pollution
1.1 Legislation .................................................. 2
1.2 Volatile organic compounds .................................. 3
1.3 Control techniques ........................................... 3
  1.3.1 Process and equipment modification ................. 5
  1.3.2 Add-on-control techniques ......................... 5
    Recovery of VOCs .......................................... 5
    Destruction of VOCs ...................................... 6
Conclusions .................................................... 8

## 2 Biofiltration: mechanism and principles ........................................... 9
2.1 Basic principles ............................................. 9
2.2 Microbiology ............................................... 10
2.3 Mass transfer ............................................... 14
2.4 Environmental factors ...................................... 15
2.5 Performance Parameters .................................... 16
2.6 Applications ................................................ 17
  2.6.1 Pollutants ............................................. 18
  2.6.2 Industrial Application ............................... 18
Conclusions .................................................... 20

## 3 Bioreactors for waste gas treatment ............................................. 21
3.1 Conventional biofilter ...................................... 21
  3.1.1 Biofilter design ...................................... 21
  3.1.2 Biomass .............................................. 21
  3.1.3 Moisture .............................................. 23
  3.1.4 Biofilter media ...................................... 23
  3.1.5 Advantages and disadvantages ..................... 24
3.2 Biotrickling filter .......................................... 24
  3.2.1 Biotrickling filter design ......................... 25
  3.2.2 Packing material .................................... 25
  3.2.3 Biomass .............................................. 26
    Biomass control .......................................... 26
  3.2.4 Trickling water ...................................... 27
Air pollution has become a more alarming problem throughout the ages. Human industrial, rural and domestic activities generate some chemical products that can modify the characteristics and the composition of the atmosphere. Some of them are also considered responsible for the change in the world climate. Such air pollutants can be transferred also in soils and in both surface and ground water, and they can be also accumulated in the biological tissues. Air contaminants contribute therefore to the overall earth-pollution. Many air pollutants act as catalyst for the ozone and smog formation in the lower layers of the atmosphere; moreover they can contribute to the depletion of ozone layer. Some of them are carcinogenic; some others can cause diseases to central nervous system, to liver and kidney.

EPER, the European pollutant emission register, subdivides the main atmospheric pollutants in some categories, to evaluate the overall emissions into air and water: methane (CH$_4$), carbon monoxide (CO), carbon dioxide (CO$_2$), hydrofluorocarbons (HFCs), nitrous oxide (N$_2$O), ammonia (NH$_3$), non-methane volatile organic compounds (NMVOCs), nitrogen oxides (NO$_x$), perfluorocarbons (PFCs), sulphur hexafluoride (SF$_6$), sulphur oxides (SO$_x$).

In the last years, an increasing interest has been developed to control air emissions. European Union has proclaimed more and more stringent limits and every European country has studied its own legislation to contrast air pollution. Many research activities have focused on the different techniques for air pollution control, creating new methods and improving the existing ones. Many studies have concerned solid-gas separation, in order to reduce the amount of fine particles in the waste gases: settling chambers, filters, electrostatic filters, cyclones, scrubbers are examples of very used equipment.

The control of Volatile Organic Compounds (VOCs) emissions have been also studied. Many processes have been developed to cover a wide range of pollutants, concentrations and flow rates. Among these techniques, biofiltration has been demonstrated to be a promising, effective and economical technique and many studies have been carried out all over the world to investigate its mechanism, to enlarge its range of applicability and to determine the engineering parameter to allow its successful application in the industry.
1. Air pollution

1.1 Legislation

European Union has proclaimed a growing number of regulations, protocols and guidelines on environmental conservation.

Moreover, it has instituted a register, EPER, *European Pollutant Emission Register*, to estimate the overall emissions for different air and water pollutants and for different industrial activities. Reports were published in 2004 and 2007. EPER register will be substituted by E-PRTR, *European Pollutant Release and Transfer Register* in 2008.

European Union established that every country has to contribute to reduce emissions. Information about pollution has been taken into great consideration as a powerful vector to make population aware on pollution risks.

**Italian legislation** All the rules on environmental conservation have been collected in the *legislative decree* number 152, 3rd April, 2006. Part V of this text deals with air conservation and air emission control.

In particular, VOC is here defined (Title I) as such organic compound which has a vapour pressure equal or higher than 0.01 kPa at 293.15K, or which has an equivalent volatility in particular employment conditions.

Limit values are also reported. Air pollutants are collected in several groups depending on the toxicity or the carcinogenic or mutagen power and also on their physical state (gas or solid). Every group is divided into different classes, depending on the compound hazardousness. Reported limits refer to the concentration of the pollutant in the waste and to the overall pollutant flow rate measured before any emission-control facility (relevance threshold). Table (1.1) reports limit values for some air pollutants.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Relevance threshold [g/h]</th>
<th>Emission values [mg/Nm3]</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>25</td>
<td>5</td>
<td>Class III, carcinogenic substances</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>50</td>
<td>5</td>
<td>Class II, inorganic gaseous substances</td>
</tr>
<tr>
<td>Ammonia</td>
<td>2000</td>
<td>250</td>
<td>Class IV, inorganic gaseous substances</td>
</tr>
<tr>
<td>Ethylmercaptane</td>
<td>25</td>
<td>5</td>
<td>Class I, gaseous organic compounds</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>100</td>
<td>20</td>
<td>Class II, gaseous organic compounds</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>100</td>
<td>20</td>
<td>Class II, gaseous organic compounds</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>100</td>
<td>20</td>
<td>Class II, gaseous organic compounds</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2000</td>
<td>150</td>
<td>Class III, gaseous organic compounds</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2000</td>
<td>150</td>
<td>Class III, gaseous organic compounds</td>
</tr>
<tr>
<td>Toluene</td>
<td>3000</td>
<td>300</td>
<td>Class IV, gaseous organic compounds</td>
</tr>
<tr>
<td>Xylenes</td>
<td>3000</td>
<td>300</td>
<td>Class IV, gaseous organic compounds</td>
</tr>
<tr>
<td>Acetone</td>
<td>4000</td>
<td>600</td>
<td>Class V, gaseous organic compounds</td>
</tr>
<tr>
<td>Hexane</td>
<td>4000</td>
<td>600</td>
<td>Class V, gaseous organic compounds</td>
</tr>
</tbody>
</table>

Table 1.1: Emission limits for some air pollutants, as reported in the legislative decree, 152, 3rd April, 2006.
1.2 Volatile organic compounds

Volatile organic compounds (VOCs) are very common air pollutants. They are characterized by a very high volatility even at atmospheric pressure and at room temperature. Many industrial processes emit VOCs. Table (1.2) shows the overall European emission (25 countries) for different industrial activities.

The emissions from every European country is reported in table (1.3). Data from 2001 and 2004 are here compared. Although European union has explicitly declared its aim to reduce emissions and prevent air pollution since 2001, some country showed an increase in the volume of non-methane VOCs released in the atmosphere: Italy is one of them.

VOCs are very hazardous compounds, since they have been demonstrated to be responsible of photochemical smog, and to cause some human diseases. Benzene has also been demonstrated to be carcinogenic.

**Effects on atmosphere** In the lower atmospheric layers, sun beams can catalyze the formation of some organic radicals from VOCs which can convert NO to NO$_2$. NO$_2$ can be subsequently degraded by a photolytic reaction, generating ozone.

Ozone is a component of the photochemical smog and it is mainly produced in summer, thanks to an increase of sun beam power. Ozone is a strong oxidizer and readily reacts with animal and plant tissues. It can irritate mucous membranes, cause caught and thorax pains, even at concentration close to 0.01 ppm.

**Effects on biosphere** VOCs are mainly persistent pollutants. They are also lipophilic and can accumulate into adipose tissues, coming into the food chain. Such a process is called bioaccumulation.

Living beings can get in contact with VOCs also from a water source. Indeed, such air pollutants can be transferred by atmospheric events into soils, surface and ground waters.

**Effects on human health** Human beings can assume VOCs by inhalation, ingestion or by skin contact. Since the wide employment of such compounds, assumption can be frequent. Many disturbs in the central nervous system have been identified: headache, dizziness, sleepiness, sickness, disturbs at coordination and equilibrium are the most common symptoms.

If direct contact occurs, VOCs can irritate the membrane tissue. A prolonged contact may cause irreversible damages at kidney and liver. Benzene can also cause malfunctioning in emopoiesis.

1.3 Control techniques

Since air pollution is a more and more outcoming, many techniques have been developed to reduce gaseous emissions. These techniques can be classified in to two main groups: process and equipment modification and add-on-control techniques [69]. The latter can operate both via pollutants destruction or recovery.

The choice of the most suitable technique depends on the flow rate, the pollutants characteristics and concentration. Application range of the various technologies applied to VOCs removal are represented in figure (1.1).
1. Air pollution

<table>
<thead>
<tr>
<th>Activity</th>
<th>Emissions [kg/year]</th>
<th>Percentage [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral oil and gas refineries</td>
<td>209 301 000</td>
<td>37.61</td>
</tr>
<tr>
<td>Surface treatment or products using organic solvents</td>
<td>121 116 000</td>
<td>21.76</td>
</tr>
<tr>
<td>Basic organic chemicals</td>
<td>105 721 000</td>
<td>19.00</td>
</tr>
<tr>
<td>Metal Industry</td>
<td>29 402 000</td>
<td>5.28</td>
</tr>
<tr>
<td>Pulp, paper or board production</td>
<td>22 415 000</td>
<td>4.03</td>
</tr>
<tr>
<td>Pharmaceutical products</td>
<td>18 143 000</td>
<td>3.26</td>
</tr>
<tr>
<td>Disposal of non-hazardous waste and landfills</td>
<td>10 134 000</td>
<td>1.82</td>
</tr>
<tr>
<td>Slaughterhouses, milk, animal and vegetables raw material</td>
<td>9 424 000</td>
<td>1.69</td>
</tr>
<tr>
<td>Combustion installation &gt;50MW</td>
<td>9 084 000</td>
<td>1.63</td>
</tr>
<tr>
<td>Basic inorganic chemicals or fertilisers</td>
<td>7 639 000</td>
<td>1.37</td>
</tr>
<tr>
<td>Cement, lime, glass, mineral substances or ceramic products</td>
<td>4 926 000</td>
<td>0.89</td>
</tr>
<tr>
<td>Biocides and explosives</td>
<td>3 763 000</td>
<td>0.68</td>
</tr>
<tr>
<td>Coal gasification and liquefaction plants</td>
<td>3 091 000</td>
<td>0.56</td>
</tr>
<tr>
<td>Pretreatment of fibres or textiles</td>
<td>911 000</td>
<td>0.16</td>
</tr>
<tr>
<td>Disposal/recovery of hazardous or municipal waste</td>
<td>561 000</td>
<td>0.10</td>
</tr>
<tr>
<td>Tanning of hides and skins</td>
<td>496 000</td>
<td>0.09</td>
</tr>
<tr>
<td>Production of carbon or graphite</td>
<td>289 000</td>
<td>0.05</td>
</tr>
<tr>
<td>Disposal or recycling of animal carcasses and animal waste</td>
<td>124 000</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Total 565 500 000

Table 1.2: Non methane-VOCs emissions in different industrial activity in the EU (25 members) [41]. Data refers to 2004.

<table>
<thead>
<tr>
<th>Country</th>
<th>Emissions 2001 [kg]</th>
<th>Percentage [%]</th>
<th>Emissions 2004 [kg]</th>
<th>Percentage [%]</th>
<th>Variation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>4 200 000</td>
<td>0.77</td>
<td>4 317 000</td>
<td>0.83</td>
<td>+2.79</td>
</tr>
<tr>
<td>Belgium</td>
<td>45 658 000</td>
<td>8.34</td>
<td>37 114 000</td>
<td>7.14</td>
<td>-18.71</td>
</tr>
<tr>
<td>Denmark</td>
<td>3 000 000</td>
<td>0.55</td>
<td>3 698 000</td>
<td>0.71</td>
<td>+23.27</td>
</tr>
<tr>
<td>Finland</td>
<td>8 228 000</td>
<td>1.5</td>
<td>1 1258 000</td>
<td>2.17</td>
<td>+36.83</td>
</tr>
<tr>
<td>France</td>
<td>132 325 000</td>
<td>24.18</td>
<td>115 296 000</td>
<td>22.18</td>
<td>-12.87</td>
</tr>
<tr>
<td>Germany</td>
<td>42 517 000</td>
<td>7.77</td>
<td>38 305 000</td>
<td>7.37</td>
<td>-9.91</td>
</tr>
<tr>
<td>Greece</td>
<td>5 031 000</td>
<td>0.92</td>
<td>8 138 000</td>
<td>1.57</td>
<td>+61.76</td>
</tr>
<tr>
<td>Ireland</td>
<td>121 000</td>
<td>0.02</td>
<td>299 000</td>
<td>0.06</td>
<td>+147.11</td>
</tr>
<tr>
<td>Italy</td>
<td>49 144 000</td>
<td>8.98</td>
<td>51 867 000</td>
<td>9.98</td>
<td>+5.54</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>280 000</td>
<td>0.05</td>
<td>288 000</td>
<td>0.06</td>
<td>+2.86</td>
</tr>
<tr>
<td>Netherlands</td>
<td>13 239 000</td>
<td>2.42</td>
<td>1 4726 000</td>
<td>2.83</td>
<td>+11.23</td>
</tr>
<tr>
<td>Portugal</td>
<td>5 604 000</td>
<td>1.02</td>
<td>17 402 000</td>
<td>3.35</td>
<td>+210.53</td>
</tr>
<tr>
<td>Spain</td>
<td>64 979 000</td>
<td>11.87</td>
<td>76 242 000</td>
<td>14.67</td>
<td>+17.33</td>
</tr>
<tr>
<td>Sweden</td>
<td>28 696 000</td>
<td>5.24</td>
<td>27 913 000</td>
<td>5.37</td>
<td>-2.73</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>144 264 000</td>
<td>26.36</td>
<td>112 863 000</td>
<td>21.72</td>
<td>-21.17</td>
</tr>
</tbody>
</table>

Total 547 286 000

Table 1.3: Non methane-VOCs emissions in the European countries in 2001 and 2004 [41]. Variation refers to the percentage difference between 2001 and 2004.
1.3. Control techniques

1.3.1 Process and equipment modification

VOCs emissions can be limited by the utilization of more environmental-friendly processes, by the improvement of their efficiency, by the reduction of material losses and also by the choice of purer raw materials.

A better mass balance study may reduce VOCs escapes in valves, pumps or pipelines; the employment of caps or close tanks can be used to collect vapours.

Process modification can not be always possible, since other technologies are not available or they are too much expensive.

However, all these expedients allow an optimum control of emissions and their contribute to the overall air pollution cannot be underestimated.

1.3.2 Add-on-control techniques

Recovery of VOCs

Such techniques are very useful with expensive compounds and they have the advantage to allow the reuse of pollutants in the process chain.

- **Condensation**  
  VOCs can be separated from other uncondensable gases by an increase in the pressure, a reduction of temperature or both. Condensation systems can use different cooling fluid or different contact system.

  This technique is used for pollutants with a boiling point lower than 40°C and for concentration higher than 5000 ppm. It is also employed as pre-treatment for other processes.

  Efficiency higher than 96% can be reached with very concentrated streams and moderate flow rates.
• **Absorption** Absorption is used to remove gaseous pollutants by transferring them into a liquid non-volatile phase.
   Efficiency basically depends on the solubility of the compounds and on the gas-liquid interfacial area, and it can be higher than 95% when flow rate ranges from 40 to 2000 m$^3$/h and VOC concentration from 500 to 5000 ppm.
   To allow a sufficient wide interfacial area, plate columns, packing columns or mist scrubbers have been used.

• **Adsorption** Adsorption is a mass transfer of a species from a fluid phase to a solid surface.
   The interaction between adsorbent and adsorbate can be *physical*, when it is based on weak Van der Waals forces, or *chemical* when a chemical reaction occurs. Physical adsorption is preferred because of its equilibrium reversibility.
   Adsorption units can be employed to treat fluxes with a wide range of concentrations (from 10 to 10000 ppm), ensuring to not exceed 25% of the lower explosive limit. An adequate adsorber can remove more than 95% of gaseous pollutants.
   The most used adsorbent carriers are *activated carbon* and *zeolites*.
   Activated carbon can be employed for several VOCs, because it is non selective, it has high porosity and high retentive properties. Moreover it can be easily desorbed. Moisture content can critically affect adsorption effectiveness since water competitively fills the active centers reducing the retentive ability. Active carbon is not effective with high boiling solvents, since regeneration is not fully possible.
   Zeolites are inorganics crystalline materials constituted by aluminium, silicon and oxygen. They are synthetically produced and the pores diameter can be fixed *a priori* depending on the crystalline structure. Zeolites become therefore selective for a specific pollutant or range of pollutants. Zeolites is safer than active carbon and easily to be regenerated, but its much more expansive.

• **Membrane technology** Membranes have been widely employed in several industrial separation processes. Membranes techniques differ from the driving force and the transport mechanism.
  *Gas permeation* and *reverse osmosis* are the technologies applied in gas recovery which are based on diffusional transport.
  Membranes are very effective but they are expensive and not easily available. Moreover bacterial growth, fouling or moisture may reduce their effectiveness.

**Destruction of VOCs**

Incineration and biofiltration are both techniques which operate the degradation of VOCs to simpler compounds, mainly carbon dioxide and water. Incineration can be *thermal* or *catalytic* with differences in the operative temperature and in the combustion chamber design.

• **Thermal oxidation** Thermal oxidation occurs in a combustion chamber at 700-1000°C. Waste air, fuel (natural gas or gasoil) and oxygen are fed to the system; VOCs concentration should never exceed 25-50% of its LEL (*lower explosive limit*) to avoid any explosion hazard. VOC inlet concentration can vary from 100 to 2000 ppm and average residence time ranges from 0.5 to 1.0 second.
Destruction efficiency depends on temperature, residence time and turbulence. Some pollutants, as halogenated hydrocarbons, require higher temperature for their complete combustion.

Thermal oxidation requires a great heat input to keep temperature high. To recover energy and reduce fuel consumption and costs, a ceramic bed can be used as heat exchanger (regenerative system). A recycle of chamber fumes to pre-heat gas inlet can also be installed (recuperative system). High VOCs concentrations are often preferred to provide a direct and significant heat amount by their oxidation.

Because the high temperatures, some toxics, as hydrogen chloride and fluoride acids, phosphene, or nitrogen oxides can be generated, which require a secondary treatment. Emissions can also contain some particulate derived from flame ashes.

Removal efficiency can be higher than 98% for most organic pollutants.

- **Catalytic oxidation**  The presence of a catalyst reduces the reaction temperature, making incineration safer and less expensive. Temperature may range between 350-500°C and VOC concentration between 100-2000 ppm.

  Catalyst are usually oxides of noble metals, as platinum, rhodium or palladium and can be easily poisoned by sulphides, chlorides and silicon. Its substitution when exhausted can strongly affect the economics of the process.

  An energy recovery is also present, since exhausted gases are used to increase inlet gas temperature before the combustion chamber.

- **Biofiltration**  Biofiltration is an out-coming technique based on the capability of some microorganisms to degrade organic matter for their own metabolism. In such bioreactors, waste gas flows throughout a packing material covered by an active biomass.

  At the beginning, biofilters were settled to remove unpleasant and noxious odours from composting and wastewater treatment plants, but their effectiveness has been further demonstrated in VOCs emission control from many industrial applications.

  Many equipments have been designed for biological VOCs oxidation and they essentially differ in the system used to supply water to the biomass.

  Biological oxidation can reach 98% removal efficiency for very biodegradable compounds and it successfully operates with high flow rates and low pollutant concentrations.

  It shows many advantages, not generating toxic by-products, working at room temperature and being cost-effective compared to the other techniques. Table (1.4) reports the most important advantages and disadvantages of biofiltration for the waste gas treatment.

  Biofiltration is the most suitable technique when gas inlet has very low pollutant concentrations and very high flow rates. In such conditions, for example, incineration would not work properly since the heat generated by the oxidation of the pollutants is negligible and, therefore, an additional amount of fuel is required to keep temperature high inside the combustion chamber.

  While other control techniques are susceptible to humidity, biofiltration can operate only if water is present. It is the best choice for the removal of odours from wastewater treatment plants, composting and breeding facilities.

  In spite of these advantages, biofiltration effectiveness is affected by biomass instability. Microorganism are indeed sensible to high concentration peaks that can abruptly reduce the
1. Air pollution

### Biofiltration

<table>
<thead>
<tr>
<th><strong>Advantages</strong></th>
<th><strong>Disadvantages</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low investment and running costs</td>
<td>• Sensible at concentration and flow rates peaks</td>
</tr>
<tr>
<td>• Operating at room temperature</td>
<td>• Long start-up period</td>
</tr>
<tr>
<td>• Effective at high humidity levels</td>
<td>• Lack of knowledge</td>
</tr>
<tr>
<td>• Effective at low concentrations and high flow rates</td>
<td>• Sensible at climatic changes</td>
</tr>
<tr>
<td>• Safe</td>
<td></td>
</tr>
<tr>
<td>• Generation of no-toxic by-products</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.4:** Advantaged and disadvantages of biofiltration for waste gas treatment

performance of the process. Moreover, long start-up periods are required to reach the stationary state and the maximum efficiency.

Carrier compaction is a critical situation, which occurs because of an excessive moisture or biomass growth. Package should be replaced increasing the overall operating costs.

Finally, biofiltration is a relatively new technique and many aspects of this process are still unknown. Thus, laboratory investigation is still necessary for enhancing biofiltration performance.

**Conclusions** Air pollution is a present problem. VOCs are very hazardous contaminants and their emissions have to be controlled. Among the control techniques, biofiltration has excited an increasing interest since it is economic, safe and effective. However, many investigation should be carried out to improve the removal efficiency, considering that the sole compliance to the legislation limits should not be enough.
Biofiltration has been demonstrated to be an economical, safe and effective technique for gas emissions control. Thanks to the first encouraging investigations, many studies have been carried out to evaluate on which gaseous pollutants such process can be successfully employed, to determine the parameters which affect efficiency, and also to develop different design solution to obtain the desired removals.

Although interest on biofiltration has more and more increased since ’70s, many aspects of this process still remain unknown. It mainly depends on the simultaneous presence of biological, chemical, chemical-physical and thermodynamic phenomena, which all have a significant influence on process efficiency. To confirm this high complexity, no mathematical model has been developed which can give any reliable prevision data.

Moreover, comparing with wastewater treatment technology, there are no tests available to characterize the interactions between biomass and substrate (as respirometric analysis), to evaluate biomass concentration (as TS/VSS procedure) or to define the organic content in the gas stream (as BOD/COD).

Thus, even if several full-scale plants have been installed to control waste gas, laboratory test, bench- and pilot-scale experiments are still necessary for a more effective employment of this technique.

2.1 Basic principles

Bioreactors for waste gas treatment employ a biomass to operate the biological oxidation of the gaseous pollutants. Microorganisms can degrade organic matter for their own metabolism to synthesize cell constituents and new cellular material. In aerobic conditions, biomass employs gaseous oxygen O₂ as electron acceptor and obtains energy by electrons transfer from a specific carbon source. The electron transport chain occurs with main cell nutrients (glucose, acetate, etc.) as well with pollutants (benzene, toluene, chlorinated aliphatic, etc.). As products of this degradation, new cellular matter, CO₂ and water are obtained.

A schematic of the biofiltration mechanism is represented in figure (2.1). Pollutant (black points) pass throughout a carrier material which is covered by an active biofilm. Water phase is also present and it is strictly required for biomass activity. Pollutants are initially absorbed into the liquid phase and then they diffuse throughout it to reach the biofilm where the reaction takes places. The products of the reaction (clear points) are desorbed and they are flushed with the gas stream. Also adsorption on the carrier may occur, especially with organic
2. Biofiltration: mechanism and principles

Adsorption can play a very important role especially during start-up period, and its contribution to the overall removal efficiency can not be underestimated.

Figure 2.1: Schematic of the mechanism and process involved in a packed bed bioreactor for the treatment of odours and VOCs.

The different biofiltration designs basically differ because of the system to provide water inside the bioreactor. Three main equipments can be identified. Conventional biofilters (BFs) consist in a packing material covered with biomass with no continuous mobile liquid phase; inlet gas stream is humidified in an pre-humidification unit before reaching the reactor. In Biotrickling filters (BTFs), a water stream trickles throughout the packing, keeping biomass wet. Bioscrubbers (BSs) are constituted by an absorption unit and a reaction unit, where biomass is suspended into the liquid phase.

Other technologies have been employed, as membrane reactors, suspended activated sludge or combined oxidation and biodegradation, which can be much more effective for some specific purpose. Among new technologies, Foamed Emulsion Bioreactor (FEBR) seems to be very promising, especially with slightly soluble pollutants.

2.2 Microbiology

Since biomass is the “engine” of the biofiltration process, the knowledge of its behaviour, the kinetics of its metabolism, and the laws governing its growth rate have to be investigated.

Carbon and energy sources  Microorganisms from a biofiltration equipment are mainly aerobic and heterotrophs.
2.2. Microbiology

Aerobic microorganisms utilize O\textsubscript{2} as electron acceptor for their own metabolism. In a bioreactor for waste gas treatment, since a fresh gas stream containing oxygen is continuously fed, only few regions could be under anaerobic conditions. It mainly occurs when biofilm thickness increases to much, limiting oxygen diffusion throughout it to the inner biofilm layers. Some gaseous pollutants, as perchloroethylene (PCE) \cite{39}, seem to be degraded only under anaerobic conditions: some studies, however, reported PCE degradation in bioreactors \cite{54}. Anaerobic metabolism is slower than the aerobic one and the energy produced by the organic compound degradation is several times lower.

When microorganisms consume organic matter as carbon source, they are called heterotrophs. Organic matter also constitutes the electron donor of the bio-oxidation and its degradation provides energy for the synthesis of new cellular material. Sulfur oxidizing microorganisms are instead autotrophs, because they use CO\textsubscript{2} as carbon source and H\textsubscript{2}S (or other sulfur-containing hydrocarbon) as electron donor.

Some compounds, especially chlorinated organics, cannot be employed by cells as an energy source. Thus, microorganisms require some secondary substrate to induce the production of enzymes capable of degrading such pollutants. This particular transformation is called cometabolism and the additional substrate is called cometabolite.

### Nutrients

For cell growth and maintaining, biomass requires some nutrients. Microorganisms consume nutrients for the synthesis of lipids, proteins and polysaccharides, which constitute the cellular matter.

Carbon, nitrogen, oxygen, hydrogen, sulfur, phosphorus, magnesium and potassium are considered macronutrients and they are needed in concentration higher than 10\textsuperscript{−4} M \cite{102}. Micronutrients are required in concentration lower than 10\textsuperscript{−4} M, as trace elements: Fe, Cl, Mo, Zn, Cu, Mn, Ca, Na, vitamins, growth hormones are common micronutrients.

### Cellular growth and kinetics

Microorganism growth is very important in biofiltration processes. Indeed, an excessive increase in microbial population may strongly reduce bioreactor efficiency. That is because biofilm thickness increases reducing the cross sectional area, causing clogging, by-pass flows and generating higher pressure drop.

The most important biofiltration microorganisms are bacteria and fungi. Bacteria mainly reproduce with a binary fission, with a generation time that can vary from days to some minutes depending on the specie. Fungi can both reproduce by budding or by a sexual mode, with the presence of spores.

Growth rate depends on the substrate availability, on temperature, pH and the presence of toxics or inhibitory substances. Biomass yield \(Y\) [gVSS/gBOD] relates the amount of biomass generated to the amount of substrate consumed for its generation:

\[
Y = \frac{dX}{dS} \quad (2.1)
\]

where \(X\) is the biomass concentration [gVSS/l] and \(S\) the substrate concentration [g/l]. Yield is typical of the bacteria species and of the particular substrate. If substrate \(S\) is the growth-rate limiting parameter, MONOD equation may be written, where the specific growth-


rate $\mu$ [h$^{-1}$] is related to the substrate concentration:

$$\mu = \mu_{\text{max}} \frac{S}{K_S + S} \quad (2.2)$$

where $\mu_{\text{max}}$ is the maximum growth rate [h$^{-1}$] and $K_S$ the Monod’s half-velocity constant for the substrate $S$ [g/l].

When $S \gg K_S$ kinetic order approximates zero and the kinetic constant is equal to $\mu_{\text{max}}$: in these conditions, growth-rate does not depend on the substrate concentration. By the contrary, when if $S \ll K_S$, growth rate has a first-order kinetic.

Combining equations (2.1) and (2.2) an expression can be obtained where the rate of substrate consumption $r_{\text{su}}$ [g/(l·h)] is related to substrate and to biomass concentration:

$$r_{\text{su}} = -\frac{dS}{dt} = -\frac{\mu \cdot X}{Y} = -\frac{\mu_{\text{max}} X S}{Y(K_S + S)} \quad (2.3)$$

Monod’s kinetic is the most employed model to define microbiological oxidation in wastewater treatment plants and in biofiltration processes as well.

Such a model has been extended to take into consideration oxygen effects on substrate removal:

$$r_{\text{su}} = \mu_{\text{max}}X \cdot \frac{S}{K_S + S} \cdot \frac{S_{O_2}}{K_{O_2} + S_{O_2}} \quad (2.4)$$

where $S_{O_2}$ is the concentration of oxygen [gO$_2$/l] and $K_{O_2}$ is the half-velocity constant for oxygen [gO$_2$/l].

Other expressions have been developed to calculate microbial growth rate. ANDREWS proposed a kinetic model which considers also some inhibitory effect introducing an inhibitory constant $K_I$ [g/l]:

$$\mu = \mu_{\text{max}} \frac{S}{K_S + S + S^2/K_I} \quad (2.5)$$

DIXON’s model considered the combined effect of two different substrates ($i$ and $j$) to the growth rate and it can be used for cometabolic degradation:

$$\mu_i = \mu_{\text{max}} \frac{S_i}{K_i + S_i + \frac{K_i S_j}{K_j}} \quad (2.6)$$

Temperature affects microbial growth as well. Every microorganism has its specific temperature range at which its activity reaches an optimal value. Cells are called mesophiles if such an optimum temperature range is between 30°C and 45°C [9]. However, mesophiles microorganism can work even out this range, from 10°C to around 50°C. Since biofiltration is a process working at room temperature, mesophile biomass is the most common inside bioreactors.

For wastewater treatment, a correlation may be written to relate substrate consumption to the temperature:

$$r_T = r_{20^\circ} \cdot \theta^{(T-20^\circ)} \quad (2.7)$$
where \( r_{20} \) is the substrate rate at 20°C and \( \theta \) is characteristic of the treatment technique. For trickling filters, for example, \( \theta \) may vary from 1.02 to 1.08, with a typical value of 1.035 [31].

**Endogenous decay and net growth rate**  Endogenous decay is an important term to be considered in the study of growth and kinetics, and it is related to the death of cells. It is supposed to be directly proportional to biomass kinetics, so that the decay rate \( r_d \) [gVSS/h] can be expressed as follows:

\[
r_d = -k_d X
\]  

(2.8)

where \( k_d \) is the endogenous decay coefficient \([h^{-1}]\). Considering this new term, the net growth rate can be written including equations (2.3) and (2.8):

\[
r_g = -Y r_{su} - k_d X
\]  

(2.9)

**Microbial population**  Biomass inside a bioreactor may be constituted by a sole species or by a microbial consortium. For some specific purpose, a single species may grant higher removal efficiency, but it has also revealed lower stability to variations in organic load, in temperature and pH. For full-scale plants, therefore, a microbial consortium is preferred.

Biomass can be provided to the system by a specific inoculum or directly by an organic carrier. Compost, soil and wood chips may contain a wide variety of microorganisms that can adapt to the new particular conditions and select the more adequate microbial species to treat the incoming pollutants.

Fungi and bacteria are the most common microorganisms inside a bioreactor. Some protozoa can also be present and they are often required: indeed, they can use simpler microorganisms as nutrient, removing them from the reactor and controlling biomass growth (protozoa predation).

Comparing with fungi, bacteria have higher growth rate and higher substrate consumption rate. However, fungi can operate with a wider range of pollutants and have revealed higher resistance to starvation periods and different moisture and pH conditions. Moreover they can be constituted by iphae, filamentous structures, which increase the specific surface area between gas and liquid phase, improving mass-transfer rate [107].

Attached biomass constitutes the biofilm. Biofilm is a layer of cells, bonded by extracellular polymers, which covers the carrier. It is characterized by a strong heterogeneity, along its thickness [33] and also along the reactor tank. Differences are in thickness, porosity and composition as well [13, 111].

**Cell concentration**  In activated sludge plants for the wastewater treatment, biomass concentration \( X \) is usually expressed with the amount of suspended volatile solids (VSS) per unit volume.

In attached biomass processes, the estimation of the microbial concentration is rather complicate and it may be inaccurate. With moving bed biological reactors (MBBR), biomass is estimated by differences in the weight of some dry carrier elements before and after a cleaning process, used to remove all the biofilm [7].
Kennes and Veiga [67] reported some techniques used to evaluate biomass concentration inside biofilters and biotrickling filters. They are mainly based on the dispersion of the attached biomass by sonication and vortexing in a known volume of water. After that, plating count was used to enumerate the cells. Other techniques involve the estimation of dry mass content by difference in weight or protein concentration.

However, all these techniques cannot be fully representative of the biomass concentration inside a bioreactor, also because they cannot take into account the stratification effects along the bed.

2.3 Mass transfer

Gaseous pollutants have to be absorbed into the water phase before reaching the active biofilm. Therefore, mass transfer phenomena play a very important role in biofiltration efficiency, and they can also represent the process rate-determining step.

**Absorption** Gas liquid equilibrium can define the conditions occurring on the surface separating the two phases. Since contaminant is present in low concentration, it can be considered diluted in the gas stream and Henry’s law can be written:

\[ C_g = H' \cdot C_l \]  \hspace{1cm} (2.10)

with \( H' \) Henry’s constant and \( C_g, C_l \) concentration of the species respectively in the gas and in the liquid phase.

Henry’s constant depends on the characteristics of the pollutants: a hydrophilic compound has a very low constant values (even \( 10^{-7} \) for phenol) compared to a hydrophobic one (\( 10^{-2} \) for trichloroethylene).

However, equilibrium conditions never occur inside a waste gas reactor, since high gas streams are required to reduce biofiltration costs. It is useful to write the mass transfer rate using bulk concentration according with the two films theory:

\[ \frac{dC_l}{dt} = k_t \left( C^* - C_l \right) = k_t \left( \frac{C_g}{H'} - C_l \right) \]  \hspace{1cm} (2.11)

\( k_t \) is the mass transfer coefficient \([h^{-1}]\), whose value depends on the pollutants properties and especially on the interfacial area and \( C^*_l \) is the concentration of the liquid saturated with the pollutant \([g/m^3]\).

In biofiltration, the highest contribute to the overall mass transfer resistance is due to the water phase. Indeed, gas film thickness is limited by the high turbulence in the gas flow. This condition becomes more marked when working with low soluble pollutants or compounds with high Henry’s constant values.

Operating with an organic carrier or simply with some suspended microorganisms, water phase contains a lot of impurities. Such impurities modify the interfacial behaviour, increasing activity, generating fluid circulation and reducing mass transfer coefficients. Because this effect, called Marangoni’s effect, the determination of \( k_t \) or Henry’s constant is often not possible [74].
2.4. Environmental factors

**Diffusion**  After being sorbed into the water phase, pollutants diffuse throughout it to reach the biofilm. Diffusion process can be described by Fick’s law and it can be expressed by the following equation:

\[
\frac{\delta C_I}{\delta t} = D \cdot \frac{\delta^2 C_I}{\delta x^2}
\]  \hspace{1cm} (2.12)

where \(x\) is the direction of the diffusion, perpendicular to the interface area, and \(D\) the diffusion coefficient \([m^2/h]\), characteristic of the couple pollutant/solvent.

Diffusion coefficient is a function of the temperature (Arrhenius’s law dependence), pressure, composition and polarity of the species.

**Adsorption**  Adsorption is the mass transfer from a fluid phase to a solid surface. According to this definition, adsorption rate is strongly depending on specific surface area and also on the adsorption capacity of the carrier. Pollutants may be adsorbed into the biofilm and also into the packing: therefore, both chemical and physical adsorption occur in biofiltration processes.

Many equations can be written to describe adsorption. Such equations refer to equilibrium isothermic conditions. Langmuir’s isotherm was obtained considering a limited number of sites and neglecting interaction among adsorbed species and it can be expressed by:

\[
C_{\text{ads}} = \frac{C_{\text{max}} \cdot C_I}{K_L^{\text{ads}} + C_I}
\]  \hspace{1cm} (2.13)

with \(C_{\text{ads}}\) pollutant concentration on the adsorbent surface per gram of adsorbent \([g/g]\), \(C_{\text{max}}\) the maximum adsorbed concentration for Langmuir’s isotherm \([g/g]\) and \(K_L^{\text{ads}}\) Langmuir’s isotherm constant \([g/m^3]\).

Freundlich proposed a widely used expression to describe adsorption:

\[
C_{\text{ads}} = K_F^{\text{ads}} \cdot C_I^{1/n}
\]  \hspace{1cm} (2.14)

with \(n\) and \(K_F^{\text{ads}}\) constants of Freundlich isotherm. \(n\) is normally around 1. In this model there is no theoretical limit to adsorption and adsorbed concentration may increase approximately linearly with liquid bulk concentration.

2.4 Environmental factors

Temperature, pH and water content strongly affect the process and their strong variations from the optimum may cause malfunctioning.

**Temperature**  Biofiltration mainly operates at room temperature and that is one of the greatest advantage of this technique. Bacteria are therefore mainly mesophils, operating between 25-40°C, with an optimum at 37°C.

Temperature variation has both positive and negative effects: while the biological activity and the diffusion is promoted by an increase in temperature, the solubility of the pollutant decreases. Moreover, high temperature means also high evaporation and the humidification...
system can not be sufficient to keep the carrier completely wet, especially in conventional biofilters.

It should be noticed that bio-oxidation is an exothermic reaction and this fact can could cause some temperature variation along the biofilter.

**pH**  Optimal pH is around 7, for the biological activity. However, the pH of carrier material can be not neutral, varying from lower than 4 for peat to around 10 for some activated carbons.

pH drops can occur in biofiltration when treating H2S, nitrogen oxides or chlorinated hydrocarbons, because some of the by-products of their degradation are acidifying compounds.

**Water content**  Water content inside a biofilter should be around 40-50% on wet basis. Lower values could not allow a complete packing wetting, while higher values could reduce the mass transfer rate between gas and biofilm.

Moisture level depends on temperature and climatic conditions and its control could be difficult. Biotrickling filters have a better control on water content.

### 2.5 Performance Parameters

To evaluate the operating conditions and the efficiency of a biofiltration process, some parameters are required. Some of them are typical of bioreactors for air pollution control and they have been applied to describe all the process configurations.

**Mass Loading Rate (L)** is the mass of substance fed to the bioreactor per unit time and volume of the carrier [g/(m³·h)]. It can be expressed by:

\[
L = \frac{C_{g,in} \cdot QV}{V} \quad (2.15)
\]

with \(C_{g,in}\) the gas inlet concentration [g/m³], \(QV\) the volumetric flow rate [m³/h] and \(V\) the bed volume [m³].

**Elimination Capacity (EC)** is the amount of pollutant degraded per unit time and volume of filter material [g/(m³·h)], and it is defined by:

\[
EC = \frac{(C_{g,in} - C_{g,\text{out}}) \cdot QV}{V} \quad (2.16)
\]

where \(C_{g,\text{out}}\) is the pollutant concentration in the outflow [g/m³].

**Empty Bed Residence Time (EBRT)** is the time required by gas to cross the entire packing volume, and it is defined as:

\[
EBRT = \frac{V}{QV} \quad (2.17)
\]
2.6 Applications

Removal Efficiency (RE) is defined as the fraction of contaminant degraded by the bioreactor and it is expressed in percentage by the following:

\[ RE = \frac{(C_{g,\text{in}} - C_{g,\text{out}})}{C_{\text{in}}} \cdot 100\% \] (2.18)

Biofilter performance is usually represented plotting EC as function of L. With low organic loads, 100% of removal efficiency can be achieved and, since \( C_{\text{out}} = 0 \), \( EC \) results equal to \( L \).

As load increases, biofilter can not completely remove the pollutant and the direct proportionality between \( EC \) and \( L \) expires. The load value at which data start moving away from linearity is called critical load \( (L_c) \). For \( L > L_c \), despite an increase in the load values, \( EC \) results essentially constant. For very high loads, \( EC \) reaches its maximum \( EC_{\text{max}} \).

This behaviour can be explained supposing the existence of different mechanisms ruling the overall process. At low pollutant concentrations, mass transfer rate is moderate, since its driving force is also moderate. As pollutant passes into the liquid phase, it is immediately degraded by the biomass. In these conditions, diffusion is supposed to be the rate determining step and, with adequate EBRT, removal efficiency could be 100%.

Mass transfer is rather promoted by high concentrations. The pollutant amount reaching the liquid phase increases as inlet load increase and the mass transfer rate could be higher than the biomass utilization rate. In these conditions, biological reaction is the rate determining step of the process and elimination capacity reaches its maximum value \( EC_{\text{max}} \).

\( EC \) vs. \( L \) graph can be therefore divided in two regions: diffusion limitation area at low loads and reaction limitation area at high loads.

\( EC_{\text{max}} \) is a very important design parameter since it defines the capability of a bioreactor. Its value may vary a lot, depending on the pollutant, the biomass and on the type of bioreactor used.

It has to be noticed that the same removal efficiency could not be always achieved if working with the same load but at different \( C_{\text{in}} \). Indeed, for very low pollutant concentrations (below 0.05-0.01 g/m\(^3\)), first-order kinetics may occur and removal efficiency will subsequently decrease [36].

2.6 Applications

Biofiltration is an effective techniques for controlling emissions with high flow rates and low pollutant concentration. To date, biofiltration has been used in several industrial process, with these main objectives:

- to control odours from composting plants, WWTP and breeding facilities;
- to reduce VOC and ammonia emissions;
- to remove hydrogen sulphide from biogas.

Although bench-scale bioreactors have demonstrated high removals for several compounds, full-scale applications has been not completely successful. It may depend on the combined presence of different pollutants, on high variation in the organic load or simply a lack of knowledge of the process.

Anyway, all these mature experiences can give some useful indications for the employment of a biofiltration process.
2. Biofiltration: mechanism and principles

### Mass Loading Rate, $L$ [g/m$^3$·h]

### Elimination Capacity, EC [g/m$^3$·h]

#### EC$_{\text{max}}$

#### Critical Load

**Figure 2.2**: Plot example of $EC$ vs. $L$ data. Diffusion limitation and reaction limitation area are visible.

#### 2.6.1 Pollutants

Bench-scale tests have been carried out to remove a wide range of gaseous pollutants. Most of them are volatile organic compounds (VOC), but many studies have also investigated the degradation of inorganics compounds, mainly $H_2S$ and $NH_3$. Table (2.1) reports some examples of pollutants treated in bioreactors.

Elimination capacity may vary a lot depending on the pollutant. Alcohols and esters have shown high biodegradability compared to other organics as phenol, chlorinated compounds and polyaromatic hydrocarbons. The pollutant solubility is normally taken into account in order to make a choice of the equipment. Bioscrubbers are effective only with high soluble compounds, while biofilters are preferred with slightly soluble pollutants.

Some compounds can also generate acidifying by-products which can be accumulated onto the packing surface. pH drop may reduce biomass activity and, therefore, the overall process efficiency. This condition has been investigating working with bioreactors treating $H_2S$ and vapours containing chlorinated hydrocarbon.

#### 2.6.2 Industrial Application

Biofiltration equipments have been employed in several industrial processes. In the beginning, they were mainly used to remove odours from wastewater treatment and composting plants.

Table (2.2) reports some studies concerning the employment of full-scale bioreactors to treat industrial off-gases and wastes. Chemical industry (paintings, solvents and plastics) and food industry have widely and successfully used biofiltration.

Many problems may be encountered working with full-scale equipment. Clogging and bed compaction for long-term operation are very common malfunctions. Carrier replacement is often required and it influences biofiltration overall cost.

pH drop can reduce removal efficiency as well. pH values lower than 3 have been measured in odours-treatment biofilter after 2 years of continuous running [39].
To be effective, biofiltration should work with high gas flow rate and low pollutant concentrations. Since these are conditions at which the other techniques for air pollution control can not work properly, biofiltration often represent a good alternative to traditional and non-biological processes.
Biofiltration: mechanism and principles

<table>
<thead>
<tr>
<th>Industrial process</th>
<th>Pollutants</th>
<th>Bioreactor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food Industry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brewery</td>
<td>H₂S, odour</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Dairy Industry</td>
<td>H₂S, CH₄, NH₃, VOCs</td>
<td>Open BF</td>
<td>[67]</td>
</tr>
<tr>
<td>Potato Processing Plant</td>
<td>H₂S, CH₄, odour</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Sponge Manufacturing Plant</td>
<td>H₂S, CS₂</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Composting plant</td>
<td>NH₃, NMHC, odours</td>
<td>BF</td>
<td>[22]</td>
</tr>
<tr>
<td>WWTP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal WWTP</td>
<td>H₂S, odour</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Municipal WWTP</td>
<td>H₂S, mercaptanes</td>
<td>BS</td>
<td>[22]</td>
</tr>
<tr>
<td>Municipal WWTP</td>
<td>odour, VOCs</td>
<td>BF</td>
<td>[22]</td>
</tr>
<tr>
<td>Tobacco Industry</td>
<td>odour</td>
<td>BF-BTF</td>
<td>[22]</td>
</tr>
<tr>
<td>Wood Industry</td>
<td>VOCs</td>
<td>BF</td>
<td>[22]</td>
</tr>
<tr>
<td>Chemicals Industry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil-Vapor Extraction site</td>
<td>gasoline vapours</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Ink-Drying Systems</td>
<td>VOCs</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Flexographic Printing Plant</td>
<td>VOCs</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Coating Industry</td>
<td>VOCs</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Fabric Softener Facility</td>
<td>odour</td>
<td>Open BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Flavor and Fragrance Manufacturing</td>
<td>odour</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Painting Industry</td>
<td>VOCs</td>
<td>BTF</td>
<td>[18]</td>
</tr>
<tr>
<td>Plastic Dashboard Manufacturing</td>
<td>styrene, buthylacetate</td>
<td>BF</td>
<td>[18]</td>
</tr>
<tr>
<td>Foundry</td>
<td>ethanol, VOCs</td>
<td>BF</td>
<td>[19]</td>
</tr>
<tr>
<td>Automobile Factory</td>
<td>odour</td>
<td>BF</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Table 2.2: Some examples of biofiltration process applications in industry. NMHC: no-methane hydrocarbon

**Conclusions**  Biofiltration is a promising and effective technique to control VOC emissions. The process is characterized by a synergy of microbiological, chemical and physical-chemical phenomena which all contribute to its performance. Biomass is the engine of the process and its growth, its acclimatization capacity, and the substrate utilization rate should be promoted and controlled to achieve higher efficiencies. However, microbial community and ecology are extremely complicated and may vary a lot during operation, so far that their control could be not always possible. Mass transfer affects as well biofiltration performance and may constitute the rate determining step of the process. Hence, adsorption, absorption and diffusion should be taken into great account when operating with bioreactors. In spite of its complexity, biofilters, biotrickling filters and bioscrubbers have been widely employed not only to control VOCs, but also to remove odours and for the desulfurization of biogas. An increasing number of full-scale bioreactors have been designed and installed to treat several different pollutants: nevertheless, basic laboratory investigations are still necessary to provide a wider knowledge of the process and to obtain still higher efficiencies.
Biomass capability to reduce air pollutants from a waste gas flow has been exploited in reactors with different design configurations. The main biofiltration equipments are conventional biofilters, biotrickling filters and bioscrubber, which basically differ on the way water is provided to the system. The knowledge of their functioning is really important for the choice of the most suitable design to accomplish the specific purposes and to define the best condition at which biodegradation has to be carried out.

3.1 Conventional biofilter

Conventional biofilters (BFs) are reactors which do not have a continuous moving liquid phase. It was the first design configuration and it was initially developed for odours treatment (Pomeroy, U.S.A., 1957 [28, 67]): its utilization has been subsequently extended to a wider range of pollutants, including VOCs.

In BFs, all the water content required for the biodegradation is provided by a pre-humidification of the gas stream.

The absence of a continuous liquid stream influences the choice of the packing material. Organic carriers are often preferred because of their high retention properties for nutrients, pollutants, and water. Moreover, compaction problems due to an excessive moisture level are almost negligible. BFs are simple, economical, but any control system is not possible.

3.1.1 Biofilter design

A typical example of a full-scale biofilter scheme is represented in figure [5.1]. Gas stream normally undergoes a filtration to remove solid particulate, which can reduce packing’s lifetime. Subsequently, gas stream is humidified before reaching the bioreactor.

Gas stream can be fed both in upflow or downflow mode. Downward flow has been seen to assure a better moisture control. If pollutants generate acidifying by-products, upward flow is preferred, because such by-products can be immediately removed from the system. Open biofilter can work, of course, only in upflow mode.

3.1.2 Biomass

Since biofilter are “open” systems, biomass is normally constituted by several different microbial species. Indeed, gas flow introduces into the system dust and aerosols which may contain
spores and cells [39].

Many studies have investigated the biodegradation of a specific pollutant by a single microbial strain, obtaining very high removal efficiencies. As this selected strains were inoculated in a pilot- or full-scale plant, a decrease in the efficiency was observed [111]. This fact can be explained stating that inoculum can not compete with natural species.

However, single strain inoculum could be useful to reduce the time for biofilter acclimatization and for start-up operations [39, 67].

In full-scale plants, microbial consortium is normally preferred also because it can achieve better long-term stability and it can better withstand peaks of inlet concentration and flow.

Bacteria and fungi are the most common microorganisms inside a biofilter. Bacteria could achieve higher growth and substrate utilization rate, but they are more susceptible to pH drops and starvation periods. Fungi grow slower, but they are much more stable. Moreover, filamentous fungi can increase the specific surface and subsequently improve mass transfer from the gas to the liquid phase.

Higher microorganisms are also present. Protozoa and nematodes are very important for the maintaining of the ecosystem inside the biofilm. Indeed, they can prevent an excessive biomass growth by means of the utilization of simpler microorganisms for their metabolism (predation).

Biomass from wastewater treatment plants has been widely used in biofilters. Since it’s a concentrated and active biomass, it doesn’t require long acclimatization. Microorganisms can also be native of the packing. In particular, working with soil and compost, new biomass addition is often not necessary.

An excessive biomass growth is responsible of a lower biofilter performance. Moreover, it has been demonstrated [33] that an increase of the biofilm thickness do not correspond to an
increase of the number of viable microorganisms. The presence of this inactive biomass is normally due to a nutrient or oxygen limitation in the deepest biofilm layers.

3.1.3 Moisture

Biomass requires water for its activity. In conventional biofilter, the humidification system could not provide the necessary water amount. Additional liquid can be introduced into the system from the top of the bed, in order to maintain a good moisture level. This additional liquid is sometimes requested to provide nutrients or alkali to the system for pH control.

Some studies [97] have demonstrated that the elimination capacity is higher with higher moisture levels. An excessive water content, however, has to be avoided because it may increase the pressure drop and the resistance to mass transfer. Also oxygen transfer rate can be reduced, with the consequent development of some anaerobic regions inside the bioreactor.

Moisture level depends on the climatic conditions. Gas stream temperature and humidity affect the water concentration inside the bed. Evaporation effects can be strong in open biofilters in the warmer seasons. Even biomass activity, since it is exothermic, can generate some dry regions with a subsequent reduction in the removal efficiency.

Moisture level strongly affects biofilter efficiency and it is mainly responsible of malfunctions [8].

3.1.4 Biofilter media

Conventional biofilters are characterized by a packing covered with an active biomass.

Beside providing a good support for microbial growth, the carrier makes the contact between pollutants and the microorganisms easier.

A good biofilter media should have a sufficient mechanical resistance and a low bulk density, an adequate porosity, good buffer and water-holding capacity. Moreover, it should be odourless and a good nutrient reservoir, to reduce further nutrients additions.

Compost, peat, wood chips, soil, activated carbon, perlite and synthetic material are the most employed media in biofilters [39].

Organic media are normally preferred since they can better retain water and nutrients, reducing additional water request.

The degradation of the carrier is a critical aspect in the operation of a biofilter, since it has been demonstrated to be responsible of the reduction in biofilter efficiency during long-term operations.

Compost  Compost is a very heterogeneous material which is obtained by the aerobic decomposition of organic stuffs. Besides having good media properties, it has a good and well-developed microbial population by itself. It has been demonstrated that compost-based bed assures better removal efficiencies compared with granulated activated carbon packing [2, 50]. Moreover, it generates low pressure drops and it is economically convenient.

In full-scale biofilters, compost replacement occurs usually every 2-5 years [16].

An excessive moisture level inside the media should be avoided. Indeed, in these conditions, bed compaction may occur, causing clogging and channeling with a high reduction in the removal efficiency. To reduce the risk of media compaction, compost can be mixed with wood chips, perlite, wood bark or an inert carrier.
Scarce moisture content has been seen to reduce biofilter performance as well, since some packing areas could be excessively dried-up with the consequent biomass deactivation.

**Inert carrier**  Inert carrier is often preferred since it has a good mechanical resistance and the risk of bed compaction is strongly reduced. Although its cost is much higher than organic media, its deactivation is less frequent and it can thus be employed for longer periods.

The most common inert packings are activated carbon, ceramic beads, lava stone, perlite, glass, vermiculite, polyurethane foam, polypropylene Pall rings [65].

Inert materials can retain low amounts of nutrients and water: therefore, they are preferably employed in biotrickling filters, where the mobile liquid phase can provide additional nutrients amount..

### 3.1.5 Advantages and disadvantages

Conventional biofilters are simple and economical. They have been widely and successfully employed for the removal of odours from wastewater treatment plants and composting plants. These waste gases have normally high humidity level, thus pre-humidification is not required.

In despite of their simplicity, BFs control is really very difficult, since their performance is strongly affected by climatic and environmental changes and no parameter can be determined to evaluate the conditions inside the bed. pH drop, nutrients lack, and non-homogeneous moisture content are not detectable and they can strongly reduce biofilter efficiency.

<table>
<thead>
<tr>
<th>Conventional Biofilters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td>Simple operation</td>
<td>Non homogeneous moisture level inside the bed</td>
</tr>
<tr>
<td>Low investment and running costs</td>
<td>Air channelling</td>
</tr>
<tr>
<td>Low water film resistance</td>
<td>Fast deactivation of the packing</td>
</tr>
<tr>
<td>Effective with odour treatment</td>
<td>Sensible to climatic changes</td>
</tr>
<tr>
<td>Good removal efficiency with low soluble pollutants</td>
<td>pH and nutrients control not possible</td>
</tr>
<tr>
<td></td>
<td>EXcessive biomass elimination not disposable</td>
</tr>
</tbody>
</table>

**Table 3.1:** Advantages and disadvantages related with the utilization of Conventional Biofilters.

### 3.2 Biotrickling filter

Biotrickling filters (BTFs) are characterized by a continuous aqueous phase trickling throughout the reactor bed. Even if working principles are the same compared with conventional biofilters, the presence of a trickling liquid imposes some different design conditions.
Trickling liquid increases the risk of bed compaction. For this reason, the packing is normally constituted by inert or synthetic material and the control of the pH, nutrients, presence of toxics is allowed by the analysis of the trickling solution which is normally recirculated.

Trickling liquid is also a good mean to remove toxic or acidifying by-products from inside the bed.

In many cases, biotrickling filters have been shown to be more effective than conventional biofilters, and, in spite of their higher operational and initial costs, they are often preferred.

3.2.1 Biotrickling filter design

A schematic biotrickling filter is represented in figure 3.2. Water phase can provide the right moisture content for biomass activity and no pre-humidification system is required. Also some mechanical pre-treatment to remove dust, ashes or grease is not necessary since the water phase is an useful mean to remove them from inside the bed.

Gas flow can be co-current or counter-current respect to the liquid phase, and there is no experimental data indicating which is the best configuration. In despite of an increase in the mass transfer rate, counter-current efficiency is affected by the presence of a big amount of pollutants recirculated at the top of the reactor with the recycled liquid. Encountering an upward clean gas flow, solute pollutant can be easily stripped, reducing bioreactor performance. For this reasons, down-ward flow is usually preferred.

The water pump for the recycling of the leachate is a critical aspect in the employment of biotrickling filters, especially with full-scale plants [115].

![Figure 3.2: Typical scheme of a biotrickling filter with a down-ward flow.](image)

3.2.2 Packing material

In biotrickling filters, inert packing is normally preferred. Such carrier has good mechanical properties, low weight and chemical stability. Moreover, it is suitable for the biomass
 attachment.

Clogging problem is much more serious in biotrickling filters than in conventional biofilters. That is due to biomass growth, which can reduce the cross-sectional area, increasing the pressure drop throughout the reactor.

Lava rock, plastic rings, activated carbon, ceramics rings, polyurethane foams and perlite are the most used packing materials.

Inert packings have the disadvantage to require biomass inoculum, to have low nutrients and water retention properties, and to have lower specific surface area.

3.2.3 Biomass

Since they are usually filled with inert carrier, biotrickling filters normally require a biomass inoculum. Microorganisms can come from other biotrickling filters, from wastewater treatment plants or from a laboratory selection and culture.

Start-up period is strongly correlated to biomass origin. Pure cultures or cultures pre-selected with the pollutant of interest have shown shorter times to reach the maximum efficiency, compared with activated sludges. After start-up period, activated sludges have revealed better resistance to inlet disturbs and higher stability in long-term operations.

Fungi and bacteria are both used, but also higher microbes are normally presents. Since the system is open and contamination is possible, pure culture in biotrickling filters are often substituted by a mixed biomass. Fungi have shown higher removal efficiency, especially with hydrophobic pollutants.

Biomass control

Biomass growth is a problem when long-term operations are planned. Since they have big amount of nutrients at their disposal, microorganism can grow fast, reducing the cross-sectional area. Many studies have investigated different system to control biomass growth, including chemical, biological and physical-mechanical techniques. However, all these techniques partially or temporarily reduce biotrickling filter performance.

It should be noticed that all the techniques here reported have been applied only in laboratory tests, and their real effectiveness on full-scale plants should be still tested.

Mechanical removal Mechanical removal includes backwashing and periodic stirring of the carrier. These techniques are simple and effective but also very expensive. Moreover, backwashing can be applied only with no-fluidizing packing.

After any mechanical removal, biotrickling filters require some days to reach the elimination capacities they had before the treatment.

Backwashing has been used for conventional biofilter as well.

Chemical control The introduction of some chemicals into the trickling liquid has been used to remove biomass from the biotrickling filter.

First attempts were carried out with NaOH solution in toluene degrading bioreactor. NaOH (0.1 M) was provided to the system every two weeks and 230 g of dry-weight biomass was removed. 1 day after the chemical wash, the elimination capacity was completely recovered.
Further experiments employed different mixtures of NaOH, sodium dodecylsulphate, NaN₃, NaClO, H₂O₂, ethanol, saturated iodine, NH₃ and HCO₃⁻ [22]. Many of these attempts completely deactivated the biomass. NaClO seems to be the most promising chemical.

**Nutrients limitation** Reducing the addition of some important nutrients (especially nitrogen) may be a good mean to reduce biomass growth. However, elimination capacity is strongly reduced as well [68].

**Protozoa predation** With mixed and complex biomass, besides fungi and bacteria, pluricellular microorganism are also present. Protozoa predation is an economical and environmental friendly system to control biomass growth in biofilters and biotrickling filters [68].

### 3.2.4 Trickling water

Biotrickling filters have been demonstrated to be more effective than conventional biofilter thanks to the recirculated trickling water.

Actually, the trickling water is an effective mean to control the pH inside the reactor, to introduce nutrients and additional minerals for the biomass growth and to remove any toxic or inhibiting substances from inside the packing. The control of the process results therefore easier and high elimination capacity can be achieved during long-term operation.

Unfortunately, the right amount of water can be determined only experimentally [66]. Biofilm drying should be avoided [123], but an excessive water can reduce the specific area, increasing the mass transfer resistance of the pollutants.

Operating costs are strongly affected also by the amount of substances required for the control of the process. For example, because the addition of alkali for pH maintaining, the degradation of air streams containing chlorinated compounds can be much more expensive if compared with other different waste gases [37].

Only few studies have investigated the contribute of the recycle liquid to the overall removal efficiency. Cox et al. [23] have demonstrated that the suspended biomass in the liquid has an average specific activity 20 times higher than that of the attached biomass. Moreover, such biomass does not originate from a detachment of the biofilm, but it is a result of a specific growth. However, its contribute to the removal efficiency is negligible, since the very low amount of suspended biomass.

### 3.2.5 Advantages and disadvantages

Comparing to conventional biofilters, BTFs can better face the control of some parameters within the reactor, such as pH, temperature, mineral media and salinity. Thanks to the moving liquid phase, they allow also the washing-out of intermediates and products of the cellular metabolism and the supplying of nutrient media into the system. Finally, they have shown better biomass adaptation capacity.

Main problems in the employment of BTFs concern the degradation of the packing. Biomass in BTFs can grow faster than in the conventional biofilters; this may cause the reduction of the packing specific area, generating clogging problems, the formation of anaerobic areas and, therefore, a sensible decrease in the removal efficiency.
Moreover the liquid film could represent an additional resistance for poorly soluble compounds, so mass transfer between gas and liquid phase could represent the \textit{rate-determining-step} of the process.

<table>
<thead>
<tr>
<th>\textbf{Biotrickling filters}</th>
<th>\textbf{Advantages}</th>
<th>\textbf{Disadvantages}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simple and flexible design</td>
<td>Adsorption may be the \textit{RDS} of the process</td>
</tr>
<tr>
<td></td>
<td>pH, temperature, salinity, and mineral media control</td>
<td>Excessive biomass growth can cause clogging</td>
</tr>
<tr>
<td></td>
<td>High EC for H$_2$S</td>
<td>Media requires replacement</td>
</tr>
<tr>
<td></td>
<td>Better biomass adaptation capacity</td>
<td>Pilot- and Full-Scale plant still developing</td>
</tr>
<tr>
<td></td>
<td>Washing-out of intermediates, by-products, toxics</td>
<td>More expensive and complex than Conventional Biofilter</td>
</tr>
</tbody>
</table>

\textbf{Table 3.2:} Advantages and disadvantages correlated with the utilization of Biotrickling Filters. \textit{RDS} = Rate-Determining-Step, \textit{EC} = Elimination Capacity.

### 3.3 Bioscrubbers

Bioscrubbers (BSs) are reactors in which absorption and reaction occur in two different units and they are mainly employed with high soluble and low volatile pollutants.

BSs design is simpler, since both absorption column and suspended growth bioreactor are well known processes. For the same reason, mass transfer and biodegradation can be highly enhanced.

#### 3.3.1 Bioscrubber design

Polluted gas is fed to the absorption unit. Packed columns have shown higher removal efficiency comparing with other absorbers designs. Moreover, they have very low pressure drop.

Liquid phase drags pollutant from the gas stream and conveys it to the bioreactor, which is generally represented by an activated sludge reactor. In this case, the high retention time may cause an excessive biomass growth inside the reactor.

A pumping system recirculates a fraction of the wastewater from the bioreactor to the top of the absorption tower.

Figure (3.3) shows a schematic of a bioscrubber.

#### 3.3.2 Advantages and disadvantages

Depending on the characteristics of the waste gas, the performance of the absorption and reaction units can be separately enhanced. Mass transfer can be improved by an adequate
3.3. Bioscrubbers

Figure 3.3: Typical schematic of a Bioscrubber

packaging or by increasing the number of theoretical plates; at the same way, reaction can be optimized by using a selected biomass or controlling pH and temperature.

However, the requirement of high investment and operating costs with the lack of knowledge of the process have limited the diffusion of this equipment.

Bioscrubbers

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Smaller volumes</td>
<td>• Higher costs</td>
</tr>
<tr>
<td>• Good control of the process</td>
<td>• High biomass generation</td>
</tr>
<tr>
<td>• Suitable for high pollutant concentration</td>
<td>• More complicated start-up procedure</td>
</tr>
<tr>
<td>• Good stability</td>
<td>• Effective for pollutants with a dimensionless Henry’s coefficient $&lt; 0.01$</td>
</tr>
<tr>
<td>• No problems concerning the carrier</td>
<td>• Wash-out of microorganism possible</td>
</tr>
<tr>
<td>• Well-established design</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Advantages and disadvantages correlated with the utilization of Bioscrubbers.
3.4 Other bioreactors

Besides the three main bioreactor configurations for air pollution control, many other alternatives have been developed.

Membrane technology has been applied in waste air treatment. Membrane bioreactors (MBR) are particularly effective with low soluble pollutants and the risk of clogging is completely avoided. Moreover, they are suitable to treat pollutants which require cometabolism. Other advantages are the low pressure drop and the optimal air flow distribution [67, 70]. The limit of this technology is actually the high cost of the membranes.

Also suspended-growth reactors can be used to remove gaseous pollutant, by flushing the contaminated gas stream throughout a liquid phase with an active suspended biomass. Clogging and drying problems are avoided and no anaerobic regions are present inside the reactor. The removal of toxic from the liquid phase and the treatment of poor soluble compounds are still problems [57].

Foamed Emulsion Biological Reactors (FEBRs) are quite recent equipments which employ a biological foam to increase the surface area for the mass transfer. FEBRs have been successfully tested with BTXs and high elimination capacity are also be obtained with TCE [61, 63, 93, 104]. Bed clogging and biomass drying are avoided, but the requirement of the specific surfactant to generate the emulsion strongly affects the operational costs. Foam stability problem concerns for the full-scale application of this bioreactor.

Monolith bioreactors have been tested only recently for treating toluene and methanol [58]. They involve a ceramic monolith packing for the biomass growth and for assuring high mass transfer between gas and liquid phase since they seem to develop Taylor flow inside the reactor.

To treat hydrophobic compounds, two-phase partitioning bioreactors have been developed. Organic solvent can increase the retentivity of hydrophobic pollutants [19]. The stirring system allows a good mass transfer rate between gas, the aqueous and the organic phases; clogging or drying are avoided. The organic phase can also be solid, mainly polymer beads which have high affinity to oxygen [26].

Conclusions Despite the wide variety of different bioreactors for waste gas treatment, conventional biofilters and biotrickling filters remain the most used equipments. The choice of the most suitable bioreactor depends on the characteristics and the composition of the waste gas and on the economical aspects as well. BTF seems to be the best bioreactor, since the process can be easier controlled with better performances. However, the knowledge of the characteristics of every bioreactor is really very important to individuate the critical aspects of the process and to reduce the risk of malfunctioning.
Since many different phenomena contribute to the effectiveness of a biofiltration process, no model has been yet developed which can comprehensively foresee bioreactor performance.

First attempt was conducted by Ottengraf and Van den Oever in 1983 [89]. This model simply deals with conventional biofilter at stationary state. In spite of its simplicity, this model has been widely used also by other authors [28, 39, 67, 55].

Further implementation were elaborated by several authors, to extend the results to transient conditions, to different biokinetics orders, to different equipments and to take into consideration the moisture level, the contribute of sorber, the temperature and the characteristics of the pollutants. Nevertheless, Ottengraf’s model keeps being used since it gives reliable data with a simple analytical solution.

A new Ottengraf-modified model is here proposed. The new model considers both diffusion and reaction limitations using a sole equation. Data obtained by this mathematical representation are here validated with the sensitivity analysis, in order to evaluate how the main parameters of the process may affect the biofilter performance.

4.1 Ottengraf’s model

Ottengraf’s model considers the different phenomena ruling biofilter performance: mass transfer and biological reaction. A schematic of the model is represented in figure (4.1).

At low inlet concentrations, the driving force ruling the mass transfer is limited. Therefore, the amount of pollutant which passes into the liquid phase is moderate and, as pollutant comes in contact with the biomass, it is completely degraded. In these conditions, diffusion is the rate determining step.

With higher gas concentrations, mass transfer is conversely promoted. The amount of pollutant transferred in the aqueous phase is greater and biomass could not be able to completely degrade this amount. In such conditions, the reaction limits the process rate.

Ottengraf proposed some equations to represent what occurs in the water film in these two opposite situations.

Hypothesis

1. Stationary state is supposed.
2. Biological kinetic is zero-order in respect of the substrate. Oxygen is always in excess and does not affect kinetics. Biofilm thickness is negligible in respect of the diameter of the carrier particles and its value is constant along the biofilter.

3. Two phases are considered: gas phase and (water/biofilm) phase. Pollutant diffusion in (water/biofilm) phase follows Fick's law.

4. Fluid interface equilibrium can be represented by Henry’s law.

5. Gas stream is a plug flow, with no axial dispersion.

6. One pollutant only is considered.

**Mass balance**

Pollutant concentration in the gas phase can be expressed by the following expression:

\[-U_g \frac{dC_g}{dh} = N A_s\]  \hspace{1cm} (4.1)

where $U_g$ is the superficial gas velocity [m/h], $h$ is the reactor height [m], $N$ is the flux of substrate from the gas to the liquid [g/(m$^2$·h)] and $A_s$ is the specific surface area [m$^2$/m$^3$].

Mass balance in the the water/biofilm can be written as follows:

\[D \frac{d^2C_l}{dx^2} - k_0 = 0\]  \hspace{1cm} (4.2)

where $D$ is the diffusion coefficient [m$^2$/h], $x$ is the direction perpendicular to the gas-liquid interface and $k_0$ the zero-order constant [g/(m$^3$·h)].

Such equations can be solved considering the different boundary conditions in reaction limitation and diffusion limitation assumptions.
4.1. Ottengraf’s model

Reaction limitation area

In this condition, introducing $m$ as the dimensionless air-water partition coefficient, the following boundary conditions can be used:

$$x = 0 \quad C_l = \frac{C_g}{m}$$  \hspace{1cm} (4.3)

$$x = \delta \quad \frac{dC_l}{dx} = 0$$  \hspace{1cm} (4.4)

and equation (4.2) has the following solution:

$$\frac{C_l}{C_g/m} = 1 + \frac{1}{2} \frac{\phi^2}{C_g/C_{g,in}} (\sigma^2 - 2\sigma)$$  \hspace{1cm} (4.5)

where $\sigma = x/\delta$ is a dimensionless coordinate [-] with $\delta$ the biofilm thickness [m], and $\phi$ the dimensionless Thiele number defined by:

$$\phi = \delta \sqrt{\frac{k_0 m}{DC_{g,in}}}$$  \hspace{1cm} (4.6)

Then, $N$ can be written as:

$$N = -\frac{D}{\delta} \left( \frac{dC_l}{d\sigma} \right)_{\sigma=0} = k_0 \delta$$  \hspace{1cm} (4.7)

Substituting equation (4.7) into equation (4.1) using the boundary condition $C_g = C_{g,in}$ for $h = 0$, the solution becomes:

$$\frac{C_{g,\text{out}}}{C_{g,in}} = 1 - \frac{A_s k_0 \delta H}{C_{g,in} C_g}$$  \hspace{1cm} (4.8)

with $H$ the height of the bed [m]. Bioreactor efficiency can be thus calculated as follows:

$$\eta = 1 - \frac{C_{g,\text{out}}}{C_{g,in}} = \frac{A_s k_0 \delta h}{C_{g,in} U_g}$$  \hspace{1cm} (4.9)

Elaborating equation (4.8), and solving as function of the elimination capacity, the following expression can be obtained [28]:

$$EC = EC_{\text{max}} = A_s k_0 \delta$$  \hspace{1cm} (4.10)

A critical point can be determined, supposing that $C_l = 0$ at the water-solid interface, or when $x = \delta$. Substituting this value into equation (4.3), a critical Thiele number can be determined:

$$\phi_{cr} = \delta \sqrt{\frac{k_0 m}{DC_{g,in}}} = \sqrt{2}$$  \hspace{1cm} (4.11)

When $\phi < \phi_{cr}$, reaction is the rate determining step of the process.
Diffusion limitation area

Mass balance into the (water/biofilm) phase should be now solved using different boundary conditions. Defining $\lambda$ as the distance from the interface gas/liquid at which $C_l = 0$, boundary condition (4.11) can be substituted by the following:

$$x = \lambda \quad \frac{dC_l}{dx} = 0$$ (4.12)

obtaining a new equation for the water phase:

$$\frac{C_l}{C_{g/m}} = 1 + \frac{1}{2} \frac{\phi^2}{C_g/C_{g,in}} \left( \sigma^2 - 2\sigma\frac{\lambda}{\delta} \right)$$ (4.13)

$\lambda$ can be easily determined with equation (4.13), fixing $C_l=0$ for $\sigma=\lambda/\delta$:

$$\lambda = \sqrt{\frac{2D C_g}{k_0 m}}$$ (4.14)

With this new condition, $N$ is equal to $k_0 \lambda$ and pollutant concentration in the gas phase can be calculated:

$$\frac{C_{g,\text{out}}}{C_{g,\text{in}}} = \left( 1 - A_s H \sqrt{\frac{k_0 D}{2 C_{g,in} m}} \right)^2$$ (4.15)

$EC$ is now a function of the mass loading rate and the correlation is represented by the following expression:

$$EC = L \left( 1 - \left( 1 - A_s \sqrt{\frac{k_0 D}{2m \delta m U_g}} \frac{V}{Q \sqrt{L}} \right)^2 \right)$$ (4.16)

First-order kinetic model

Further implementations were carried out to extend Ottengraf’s model also to system with a first-order kinetic. With this new assumption, mass balance in the water/biofilm phase becomes [TT9]:

$$\frac{d^2C_l}{dx^2} - k_1 C_l = 0$$ (4.17)

where $k_1$ is the first-order kinetic constant.

Solving mass balance for the gas phase, the following equation can be obtained:

$$\frac{C_{g,\text{out}}}{C_{g,\text{in}}} = \exp \left( \frac{HA_s D \phi_1 \tan \phi_1}{\delta m U_g} \right)$$ (4.18)

with $k_1$ the first-order kinetic constant [h$^{-1}$], and $\phi_1$ the Thiele’s module defined as follows:

$$\phi_1 = \delta \sqrt{\frac{k_1}{D}}$$ (4.19)
4.2 Other models

During the ages, new models have been proposed to describe biofiltration process. All this attempts are based on mass balance and introduce new elements of complexity, so that their solution can be obtained only with numerical methods.

**Summary on Ottengraf’s model**

The possibility to have at disposal an analytical solution is the strong point of Ottengraf’s model. It was the first mathematical approach to biofiltration and it was the start point for all the following models.

Its main theoretical limit is to consider that only reaction or diffusion limitation occurs in a biofilter. That’s can not be true, especially with loads close to the critical load. Moreover, zero-order kinetics can not be verified at low load values and with poorly-soluble pollutants.

**Shareefdeen and Baltzis (1993)** From Ottengraf’s results, SHAREEFDEEN and Baltzis proposed a new model, which takes into consideration also the transient conditions and the adsorption effects on the removal efficiency [101].

Oxygen diffusion throughout the biofilm and its availability for the biomass were also included, since it had been demonstrated that, with some pollutants as methanol, process may be limited by oxygen mass transfer.

Mass balance was solved using dimensionless constants and it was possible only supposing a quasi-steady-state condition for the biofilm phase. Unlike Ottengraf’s model, Shareefdeen’s solution can be obtained only with a numerical calculation.

This model was successively extended to VOC mixtures [120] using a modified Monod and Andrew’s kinetic model and introducing axial dispersion terms [121].

**Devinny and Hodge (1995)** DEVINNY and HODGE [50] proposed a dynamic model for biofilters which assumes that the mass transfer rate occurs much faster than biodegradation and
advection.

First order kinetics was assumed and two phases were considered: (solid/water) phase and gas phase. It was also supposed that, during the start-up period, the removal of pollutants is only due to adsorption and not to microbial activity.

The model can give a simple steady-state solution, neglecting all the dispersion effects:

$$C_{g,\text{out}} = C_{g,\text{in}} e^{-\frac{k_1 k_m h}{U_g}}$$  \hspace{1cm} (4.20)

with $k_1$, first order kinetic constant [h$^{-1}$], and $k_m$ ratio between pollutant amount in the (solid/water) phase and in the gas phase.

**Deshusses et al. (1995)** Deshusses et al. [30, 31] have considered also diffusion inside the biofilm. Their model is dynamic and considers three different phases: gas, biofilm, and solid.

Biological kinetics was Monod’s type without oxygen limitations and gas-liquid equilibrium is ruled by Henry’s law. Adsorption of pollutants in the solid is also included.

**Johnson and Deshusses (1997)** Johnson and Deshusses [59] tried to determine the value of $EC_{\text{max}}$ and $L_c$ as a function of the Henry’s constant, the octanol/water partition coefficient, the molecular connectivity index, and group contributions:

$$\log_{10}(EC_{\text{max}}) = \alpha H' + \beta \log K_{ow} + \gamma \chi + \sum_{\text{groups}} n\Delta$$  \hspace{1cm} (4.21)

$$\log_{10}(L_c) = \alpha' H' + \beta' \log K_{ow} + \gamma' \chi + \sum_{\text{groups}} n\Delta'$$  \hspace{1cm} (4.22)

where $H'$ is the dimensionless Henry’s constant [-], $K_{ow}$ the octanol/water partition coefficient [-], $\chi$ the molecular connectivity index [-], $n$ the number of elements of the same group which constitute the pollutant and $\alpha, \alpha', \beta, \beta', \gamma, \gamma', \Delta, \Delta'$ coefficients of the model that should be determined by fitting the experimental data.

**Ranasinghe et al. (2002)** The moisture content and the energy balance are included in the model proposed by Ranasinghe et al. [96]. Water and biofilm are considered as a one homogeneous phase, and its equilibrium with gas phase is ruled by Henry’s law.

The substrate utilization rate follows Monod’s equation with the introduction of two new factors, that are respectively affected by temperature ($T$) and moisture level ($\theta_m$).

Energy balance was realized considering the gas phase as an ideal gas and the biofilter as an adiabatic reactor.

### 4.3 Ottengraf-modified model

The model proposed by Ottengraf and van den Oever in 1983 is the first important attempt to give a mathematical approach to biofiltration process.

It is mainly based on mass balance for all the involving phases and it makes possible to determine the removal efficiency depending on the phenomena (reaction or diffusion) which
4.3. Ottengraf-modified model

rule the process. Two different equations were proposed, the one for reaction limitation area and the other for the diffusion limitation area; the transition between the two conditions is ruled by the Thiele number.

A new model is here proposed to give a mathematical continuity to the two Ottengraf’s equations. In this way, the contribute of both phenomena can be taken into consideration simultaneously. The new Ottengraf-modified model has been validated by sensitivity analysis, to assess its limits and instabilities and to determine which process parameters stronger affect the removal efficiency.

In the further chapters, model will be tested with experimental data obtained from a biotrickling filter with TCE as target pollutant.

4.3.1 Fundamentals of the new model

Ottengraf’s model individuates two different phenomena, ruling and determining the rate of the biofiltration process.

At low load values, diffusion is the rate determining step and, in such conditions, the elimination capacity is given by the following equation:

\[ EC_{dl} = L \left( 1 - \left( 1 - A_s \sqrt{\frac{k_0 D}{2m}} \sqrt{\frac{V}{Q L}} \right)^2 \right) \]  \hspace{1cm} (4.23)

where the index \( dl \) stands for diffusion limiting.

Otherwise, at high loads, the removal of the pollutant is mainly influenced by the biological reaction and the elimination capacity is load-independent:

\[ EC_{rl} = EC_{max} = A_s k_0 \delta \]  \hspace{1cm} (4.24)

But, having the use of one equation only that can continuously connect the different expression of \( EC_{dl} \) and \( EC_{rl} \) can be very useful for biofiltration design.

The following equation can satisfy this condition:

\[ EC = EC_{max} + \frac{(EC_{dl} - EC_{max})}{1 + \left( \frac{L}{L^*} \right)^2} \]  \hspace{1cm} (4.25)

where \( L^* \) is the load at which the transition between reaction and diffusion limitation occurs: for \( L < L^* \), conditions of diffusion limiting area are verified, while for \( L > L^* \) the bioreaction is the rate determining step.

For \( L \ll L^* \), the denominator of the second term on the right side becomes equal to 1 and in such conditions, \( EC \equiv EC_{dl} \).

Similarly, for \( L \gg L^* \), all the second term on the right side becomes zero and therefore \( EC \equiv EC_{rl} \).

Parameter \( p \) is calculated by fitting of the experimental data. Its value specifies the rate at which the passage between the two different limiting conditions occurs.
4. Modelling

Having a sole equation has many advantages, including the possibility to correlate directly the removal efficiency to the load and to the inlet concentration. Indeed:

$$\eta = \frac{C_{g,\text{in}} - C_{g,\text{out}}}{C_{g,\text{in}}} = \frac{EC}{L} = \left( \frac{EC_{\text{max}} + \left( EC_{\text{dl}} - EC_{\text{max}} \right)}{1 + \left( \frac{L}{L^*} \right)^p} \right) / L \quad (4.26)$$

With some arithmetical steps and using the definition of $L$ and $EC$, it is also possible to write efficiency and $C_{g,\text{out}}$ as a function of $C_{g,\text{in}}$:

$$\eta = \frac{C_{g,\text{in}}Q}{V} \left( 1 - \left( 1 - A_s V^\sqrt{\frac{k_0 D}{2mC_{\text{in}}}} \right)^2 \right)$$

$$\eta = \frac{C_{g,\text{in}}Q}{V} \left( 1 + \left( \frac{C_{g,\text{in}}}{C_g^*} \right)^p \right) \quad (4.27)$$

$$C_{\text{out}} = C_{\text{in}} - \left[ \frac{Q \cdot A_s k_0 \delta}{V} + \frac{C_{\text{in}} \left( 1 - \left( 1 - A_s V^\sqrt{\frac{k_0 D}{2mC_{\text{in}}}} \right)^2 \right)}{1 + \left( \frac{C_{\text{in}}}{C^*} \right)^p} \right] \quad (4.28)$$

where $C^*$ is the inlet concentration at which load is equal to the $L^*$, at constant flow rate and volume.

This simple modification of Ottengraf’s model is not merely an algebraical expedient to give mathematical continuity to equations (4.23) and (4.24). Indeed, it was expected that, inside a biofilter or biotrickling-filter, diffusion and reaction limitation conditions simultaneously occur. This may be due to the progressive reduction of pollutant concentration along the reactor, to the presence of some areas with different superficial velocities and to changes in the thickness of the (biomass/water) film.

However, in the new model, as inlet load increases, limitations caused by diffusion reduce and the ones caused by reaction become stronger.

Figure (4.3) compares the original Ottengraf’s model and the new modified model. Parameters used for the plotting are the same reported by Ottengraf [89] for toluene degradation.

It should be noticed that for this parameters set, the new model individuates an area with efficiency higher than 100% at very low load values. This behaviour can be likely explained by the utilization of some parameters that were obtained by Ottengraf from the fitting of his model and that can not be suitable for the new model. The arbitrary choice of the parameter $p$ could also cause this anomaly.
4.3. Ottengraf-modified model

Figure 4.3: Comparison between original Ottengraf model and Ottengraf-modified model. Parameters obtained from Ottengraf-van den Oever (1983) with toluene as target pollutant. \(A_s=501 \text{ m}^2/\text{m}^3, k_0=20 \text{ g/(m}^3\text{ h)}, \delta=1.2\times10^{-3} \text{ m, } D=8.5\times10^{-10} \text{ m}^2/\text{s, } m=0.27, \text{ EBRT}=111.1 \text{ s. } L^*=50 \text{ g/(m}^3\text{ h)}, p=1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area</td>
<td>(A_s) 501 \text{ m}^2/\text{m}^3</td>
</tr>
<tr>
<td>Zero-order kinetic constant</td>
<td>(k_0) 20 \text{ g/(m}^3\text{ h)}</td>
</tr>
<tr>
<td>Biofilm thickness</td>
<td>(\delta) 1.2\times10^{-3} \text{ m}</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>(D) 8.5\times10^{-10} \text{ m}^2/\text{s}</td>
</tr>
<tr>
<td>Air/water partition coefficient</td>
<td>(m) 0.27 -</td>
</tr>
<tr>
<td>Empty bed residence time</td>
<td>(\text{EBRT}) 111.1 \text{ s}</td>
</tr>
<tr>
<td>Inlet critical concentration</td>
<td>(C^*) 3 \text{ g/(m}^3\text{ h)}</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters from Ottengraf’s model.

4.3.2 Sensitivity Analysis

Sensitivity analysis is very useful to evaluate how parameters affect the outputs of a mathematical model. It can be also used to evaluate the quality of a model and to verify if there is a good agreement between the physics of the process and the model itself.

The main parameters to be considered are: the Empty Bed Residence Time (EBRT) [s], the biofilm thickness \((\delta)\) [m], the specific surface area \((A_s)\) [m\(^2\)/m\(^3\)], and the zero-order kinetic constant \((k_0)\) [g/(m\(^3\) h)].

Effects of the mathematical parameters \(p\) and \(L^*\) have been investigated as well.

During sensitivity analysis, only the specific target parameter is changed, while the others assume the values defined by Ottengraf [89] and reported in table 4.1. \(L^*\) was calculated by the value of \(C^*\), also suggested by Ottengraf.
When inlet concentration and gas flow rate are known, reactor volume can be essentially determined by the EBRT that is required to obtain the desired removal efficiency.

Figure (4.4) shows the combined effect of load and EBRT on the elimination capacity. As expected, an increase in EBRT leads to an increase in the elimination capacity when load is fixed.

However, since \( L = C_{in}/\text{EBRT} \), working with constant loads and variable EBRT means changes in \( C_{in} \). Thus, a better representation of EBRT effect can be obtained by plotting EC as a function of EBRT and inlet concentration (figure (4.5)). EBRT effects on efficiency are more marked at low EBRT values and high concentrations.

The new model has shown some irregularities at low inlet concentrations. Indeed in such conditions, \( \eta \) resulted even higher than 100% for some EBRT values. A peak in the removal efficiency is thus revealed for \( \text{EBRT}>200 \text{ sec} \). Figures (4.6) show the profiles of EC and \( \eta \) curves for different EBRT.

It should be noticed that the \( \eta \) peak value has a maximum at around 300 sec and than slowly decreases for higher EBRT values.

Specific Surface Area Specific surface area affects both reaction and diffusion limitation zones. This influence can be observed in a variation of the slope for low inlet concentration and in a linear variation of the asymptotic limit for high loads. Figure (4.7) reports EC and \( \eta \) vs. \( C_{in} \) for different \( A_s \) values.

A peak in the \( \eta \) values can be noticed for \( A_s >1000 \).

In biotrickling filters or in biofilters, \( A_s \) can be set by using different packings. It should be noted, that \( A_s \) depends on the moisture level and on biofilm thickness, since the effective superficial area can be strongly influenced by both of these parameters. Thus, during long-term operation, the specific surface area can be strongly decreased.

Kinetic constant Kinetic constant is linearly proportional to \( EC_{rl} \) and it affects the \( EC_{dl} \) term with a power factor of 1. Thus, comparing with \( A_s \), \( k_0 \) effects on the elimination capacity are less marked in the diffusion limitation region.

\( k_0 \) depends on the biomass/contaminant interaction and it can be varied by choosing a more suitable biomass for the target pollutant. Even changes in temperature and pH may affect the biological kinetics.

\( k_0 \) effects on EC and \( \eta \) for the Ottengraf-modified model are represented in figure (4.8).

Biofilm thickness For the Ottengraf model, \( \delta \) has effects on EC only in the reaction limitation area. Instead, the new model considers a dependence even in the diffusion limitation area, and this dependence decreases as the inlet concentration approaches zero (figure (4.9)).

The thickness used in the model refers to the active biofilm. Therefore, biomass growth does not necessary increase the elimination capacity. By the contrary, it can contribute to reduce the effective specific surface area and consequently the removal efficiency.

\( L^* \) and \( p \) \( L^* \) and \( p \) are the model parameters employed to give continuity to the two Ottengraf’s equation.

\( L^* \), however, has a physical meaning, since it represents the transition between the two different rate regimes. As shown in figure (4.10), an increase in \( L^* \) values causes a reduction in the efficiency for low inlet concentrations and an improvement for high loads.
4.3. Ottengraf-modified model

Figure 4.4: Sensitivity Analysis of Ottengraf-modified model. $L - EC$ diagram as function of the $EBRT$.

Figure 4.5: Sensitivity Analysis of Ottengraf-modified model. $C_{in} - EC$ diagram as function of the $EBRT$. 
Parameter $p$ specifies the velocity at which transition occurs. $p$ values lower than one have negative effects for low concentrations, since the contribute of $EC_{ci}$ in this area becomes more intensive. Values higher than 3 generate a peak in the $EC$. The maximum value of this peak increases with $p$ values (figure 4.11).

Parameter $p$ can be calculated only by fitting. A first-attempt value should take into account this considerations.
4.3. Ottengraf-modified model

Figure 4.8: Effects of $k_0$ and $C_{in}$ on the elimination capacity and the removal efficiency.

Figure 4.9: Effects of $\delta$ [mm] and $C_{in}$ on the elimination capacity and the removal efficiency.

4.3.3 Model advantages and limitations

Since it is based on Ottengraf studies, the model has the same limitations.

First of all, it is restricted to stationary conditions. The response of the system to external variations is thus not considered. However, it can be used for a first attempt or to evaluate how parameters vary during the operation.

In addition, the degradation rate follows a zero-order kinetic. This assumption may be valid for high inlet concentrations and for very soluble pollutants. Indeed, it has been demonstrated that for certain types of contaminants, first-order kinetic prevails [36]. Oxygen limitations are
Figure 4.10: Effects of $L^*$ [$\text{g/(m}^3\text{h)}$] and $C_{in}$ on the elimination capacity and the removal efficiency.

Figure 4.11: Effects of $p$ model parameter [-] and $C_{in}$ on the elimination capacity and the removal efficiency.

also not considered in the kinetic model.

Stratification of the biofilm along the reactor and the contribute of the moisture level are also not included in the model.

In addition, Ottengraf model dealt with conventional biofilters, hence it does not consider the effects of the trickling water on the removal efficiency.

Anyway, the Ottengraf-modified model furnishes one only equation for the entire range of mass loading rate and , thereby, many equations can be written to relate loads, concentration, elimination capacity and efficiency.
4.3. Ottengraf-modified model

Since it has an algebraic solution, it is simple to use and it may be useful for a first evaluation of the process.

It can consider both the contributes of reaction and diffusion limitation on the removal efficiency and it relates such contributes to the inlet load. Moreover, it can separate effects of inlet concentration and load on the $EC_{rl}$.

For some determined parameters set, the model can be inadequate. $\eta$ values can be higher than 100% and they can drop fast as they approach very low inlet concentrations. However the choice of a proper value for the $p$ parameter will reduce this inconsistency.

Comparing with the original model, the possibility to vary two new parameters ($L^*$ and $p$) will surely improve the quality of the fitting.

However, the main limit of the Ottengraf-modified model is that experimental data from both reaction and diffusion limitation zones are required for fitting optimization. Indeed, fitting calculation is strongly unstable when both $EC_{rl}$ and $EC_{dl}$ are not available. For some specific target pollutants, obtaining data from reaction limitation area could be not feasible, because excessive inlet concentrations.

4.3.4 Further Implementations

The model can be simply implemented by changing the mathematical equation used to pass from reaction limitation area to diffusion limitation area.

A first change may concern the exponent $p$, that can be substituted by any equation positive in all the interval. Suitable equations can be: $(aL + b)$ or $(c/L)$ with $a, b, c > 0$. Other equations, different from equation 4.25 can also be used to give continuity to the Ottengraf’s model.

The introduction of first-order or Monod-type kinetics in the model can be more suitable for some hydrophobic pollutants. This modification, however, will introduce a higher complexity in the solution of the mass balance by which $EC_{rl}$ and $EC_{dl}$ are determined.

Conclusions

Biofiltration is a very complicate process and therefore, in spite of the many attempts carried out during the ages, its mathematical representation has been not yet exhaustive. Ottengraf model is simple and reliable and it does not require numerical calculation. However, it is described by two different equations and it can not consider simultaneous effects due to reaction and diffusion limitation. Ottengraf-modified model could withstand this limits. The sensitivity analysis on this new model showed a good agreement between calculated data and the physics of the process, so far that it could represent a good mathematical mean for a preliminary process design.
Trichloroethylene (TCE) is a volatile chlorinated aliphatic compound which is commonly found in indoor air, groundwater and soils. As the other chlorinated hydrocarbons, TCE is hydrophobic and resistant to biodegradation. TCE was widely and extensively used as drying cleaning agent [27]. It still has wide applications as solvent, metal degrease, extractive solvent for olive and soybeans and as intermediate for the organic and inorganic chemical industry [27, 83].

The direct contact with TCE can be very dangerous for human beings, animals and plants even at low concentrations. For these reasons, it’s necessary to control TCE emissions in both gaseous and liquid effluents. The knowledge of the properties of the target pollutants is an essential requirement for the choice of the most suitable equipment for its treatment and for individuating the critical aspects of its removal. TCE has been seen to be biodegradable under aerobic conditions only recently. Unfortunately no microorganism has been found, which can utilize TCE as the sole carbon source. Cometabolism seems to be the only way for the mineralization of TCE in a biological reactor. Moreover, during TCE pathway, some byproducts and intermediate are produced which can deactivate the enzymes capable of TCE biodegradation. The biodegradation of TCE, as others chlorinated hydrocarbons like tetrachloroethylene (PCE), requires particular care and represents one of the most exciting challenge in waste gas biofiltration.

5.1 Chemical and Physical Properties

Trichloroethylene is a clear, colorless liquid with a chloroform-like odor. It is slightly soluble in water, but infinitely soluble in alcohol and ether. It is quite stable and can slowly decompose to hydrochloric acid when exposed to light and moisture. If heated, it can produce carbon monoxide, carbon dioxide, hydrogen chloride and phosgene.

More physical and chemical properties are listed in table (5.1).

5.2 Hazardousness

Many studies report TCE effects on human beings and animals.
Table 5.1: Physical and chemical properties of TCE.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>87°C</td>
<td>126</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-73°C</td>
<td>126</td>
</tr>
<tr>
<td>Relative density</td>
<td>1.47 (water=1)</td>
<td>126</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>1 g/l @ 20°C</td>
<td>127</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>57.8 mmHg @ 20°C</td>
<td>126</td>
</tr>
<tr>
<td>Relative vapour density</td>
<td>4.5 (air=1)</td>
<td>126</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.54 cP @ 25°C</td>
<td>126</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>4.5 @ 25°C (n-buthylacetate=1)</td>
<td>126</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>420°C</td>
<td>126</td>
</tr>
<tr>
<td>Explosive limits</td>
<td>8-12.5 vol%</td>
<td>126</td>
</tr>
<tr>
<td>Octanol/water partition coefficient</td>
<td>log $K_{ow}$ 2.42</td>
<td>127</td>
</tr>
<tr>
<td>Henry’s Law constant</td>
<td>0.0103 atm×m³/mol</td>
<td>128</td>
</tr>
<tr>
<td>Diffusion coefficient in water</td>
<td>3.75×10⁻⁶ m²/h</td>
<td>99</td>
</tr>
<tr>
<td>Air/water partition coefficient</td>
<td>0.4</td>
<td>44</td>
</tr>
</tbody>
</table>

The contact normally occurs by inhalation, ingestion or adsorption through the skin. At low concentrations or for short contact time, TCE affects the central nervous system, causing headache, dizziness, cardiac arrhythmia, unconsciousness, nausea, visual disturbance, incoordination. Test on animals revealed that it can cause cancer at liver and kidney.

Inhalation can irritate the respiratory tract. Ingestion irritates the gastrointestinal tract, causing diarrhea and abdominal pain. Fatal ingestion dose is estimated at 3-5 ml/Kg [126].

Moreover, some anaerobic bacteria can degrade TCE to Vinyl Chloride [83], which is a well-known hazardous carcinogenic compound.

5.3 TCE Production, Utilization and Emissions

TCE is a common compound widely used in industry.

Until 1970s, TCE was obtained starting from acetylene and chlorine. The reaction occurs with ferric chloride as catalyst and generates tetrachloroethane. Afterwards, tetrachloroethane is dehydrochlorinated to TCE in an aqueous solution of calcium hydroxide.

Today, TCE is produced from ethylene with two subsequent chlorinations. The first one is catalyzed by ferric chloride to generate dichloroethane. The latter occurs at 300°C and it is catalyzed by potassium and aluminium chloride to generate TCE and tetrachloroethylene as main by-products.

The main applications of trichloroethylene are represented in figure (5.1(a)).

In the 1920s and 1930s, TCE was widely used as drying cleaning agent, as extractant for food industry and to realize anesthetics and analgesics for medical purpose.
5.4. TCE Biodegradation

Nowadays, it’s commonly used as degreasing agent for metals, as solvent for adhesive paints, in the textile industry, for adhesives and lubricants and in the polyvinyl chloride production.

It is used also as a low-temperature heat transfer liquid and as intermediate for pesticides and other chemicals.

EPER, the European Pollutant Emission Register, published in June 2004 a review which reported the global European emissions for different air and water pollutants: the total amount of TCE emission was equal to 2,704,144 kilograms.

![Graph showing TCE emission in air by activity and per country.](image)

Figure 5.1: TCE emission in Europe, per country and by activity. Data from EPER, European Pollutant Emission Register, Review Report, June 2004.

5.4 TCE Biodegradation

The aerobic biodegradation of TCE has been demonstrated only in recent years. In 1984, Wilson & Wilson [116] have carried out an experiment in which biological activity of soil bacteria could reduce TCE concentration from an aqueous phase. Their result could be
achieved only if a natural gas containing methane and other small alkanes had been supplied to the system.

This suggested that there should be a cometabolic pathway which should lead to TCE degradation.

Subsequent studies mainly concerned TCE removal from groundwater and soils and many different cometabolites were used, such as methane, propane, methanol, and also aromatic chemicals like toluene and phenol.

The effect of copper ions on the microorganism activity was found to be of particular interest. Copper is common in soil and groundwater and it has been seen to reduce the expression of TCE-degrading enzymes by the cells. The investigation of the most suitable mutant, capable to be not affected by copper, became therefore very important [42, 92].

Cometabolism A deep investigation of the biodegradation process showed that the cells require cometabolite to express the enzymes capable of degrading TCE. Moreover, until to now, no microorganism, whose metabolism can use such chlorinated solvents as the sole energy and carbon source [122], has been found. Maybe it depends on the evidence that TCE oxidation cannot generate NADH (Nicotinamide adenine dinucleotide) [20], which is a very important co-enzyme for the aerobic energy production within the cells. Thus, a primary substrate or cometabolite is required for the biological oxidation of TCE.

Different primary substrates have been used, such as methane, propane, phenol, toluene. The choice of the right cometabolite mainly depends on the biomass characteristics. By the way, Sun & Wood [109] demonstrated that higher efficiency could be achieved if working with glucose as carbon source.

Because the no-specificity of these kind of enzymes, the presence of the primary substrate can develop competitive inhibition, decreasing TCE mineralization rate [20]. The right cometabolite substrate concentration were investigated by several authors [20, 60, 83], in order to find the optimum degradation rate. Misra & Gupta [83] calculated that with a primary substrate concentration 100 times higher than TCE, inhibition and toxicity of by-products are limited. Jung & Park [60] found an optimum toluene/TCE ratio of 0.3, in order to maximize TCE removal efficiency. Recent studies [60, 71] demonstrated higher removal efficiencies if the primary source is provided with a cycling feed.

Moreover, it has also been demonstrated [44] that the presence of TCE can change the kinetics of substrate degradation, introducing an inhibitory term. The kinetics can be better represented by Haldane’s expression.

Another remarkable factor effecting TCE removal is the the generation of some hazardous intermediates. Some of them, like TCE-epoxide, seem to be toxic for the microorganisms. In fact, it can spontaneously alkylate cellular components like DNA, RNA, proteins and enzymes [63]. Other studies, as reported by Zhang et al. [122], showed that acetylene can selectively deactivate some enzymes; therefore, it is necessary to remove such compounds to achieve higher efficiencies.

pH value has been seen to be very important, because TCE mineralization passes through some acid intermediates, although, until now, its effect on the removal efficiency hasn’t been deeply studied. Many studies [122, 79, 109] worked with a pH around 7.0 and Misra & Gupta [83] found an optimal pH condition at 7.4±0.2.
Enzymes  The main enzymes capable of degrading TCE are toluene *ortho*-monoxygenase (TOM), soluble methane mono-oxygenase (sMMO) and toluene dioxygenase (TDO). They are expressed by cells during the primary substrate degradation pathways.

TOM is expressed in the presence of aromatic compounds, such as toluene and phenol. sMMO is active in the presence of methane, propane, ammonia, phenol and toluene [122]. The first enzymatic attack produces TCE-epoxide which undergoes a spontaneous decomposition in aqueous phase. TDO, which is produced by toluene-oxidizing and phenol-oxidizing cells, can initially catalyze the addition of $\text{O}_2$ to an aromatic ring carbon.

Microorganisms  The main microorganisms capable of degrading TCE are *Burkholderia cepacia* G4, *Methylosinus trichosporium OB3b* and *Pseudomonas putida* F1. In the presence of different cometabolites, they can express an enzyme, TOM, sMMO and TDO respectively, which can give the first attack to TCE.

*B. cepacia* G4 can produce TOM which can be activated by the presence of aromatic compounds like toluene and phenol [109]. It can degrade TCE without generating TCE-epoxide, which is responsible to decrease enzymatic activity. Moreover it seems to be less influenced by copper ions and to have a higher TCE degradation rate [109].

*B. cepacia* has shown different behaviours if it is attached or suspended in a liquid medium [110]. Cell growth, enzyme production, nutrient uptake rate and long-term stability can vary a lot depending on biomass conditions.

*M. trichosporium OB3b* is a gram-negative bacteria which can use methane as sole carbon source; it has faster cell growth than *B. cepacia*, but it’s more affected by competition between the primary source and TCE. Its enzymes are activated by the presence of methane or other aliphatic compounds. One problem concerning the utilization of such bacteria is that it can’t adhere very well to solid surfaces [43]: biofilm can’t be therefore very thick.

*P. putida* F1 uses toluene as primary substrate as well; different strains from the same species have been widely used.

The degradation pathway of this main organism is reported in figures (5.3), (5.4) and (5.5) [125]. In all cases, the limiting step is the first attack to the chlorinated compound which generates TCE-epoxide: the following reactions seem to be spontaneous or much faster.

Besides the main mutants previously reported, other authors use different bacteria from the same species or different mutants, as *P. cepacia* [44], *P. putida* GJ31 [79], *P. fluorescens* [78], *P. mendocina* [78], *B. cepacia* PR123 [109], *M. trichosporium* PP358 [12].

Other microorganism were found to be capable of TCE degrading, MALACHOWSKY et al. [78] used *Rhodococcus* sp. for the aerobic degradation of TCE and Vinil-Chloride; other authors used *Mycobacteria vacca* which uses propane as primary source, or *Nitrosomonas europae* which is an autotrophic bacterium that can get energy from the oxidation of ammonium to nitrite [122].

Biodegradation Modeling  Many mathematical models have been developed to estimate the aerobic biodegradation of TCE and other chlorinated compounds. ZHANG et al. [122] reported several models, which are mainly based on Monod’s kinetics, introducing terms to take into account primary substrate (subscript ps) and oxygen:

$$
\frac{-dC}{dt} = \frac{\mu_{\text{max}} X}{Y} \cdot \frac{C}{K + C} \cdot \frac{C_{ps}}{K_{ps} + C_{ps}} \cdot \frac{\text{O}_2}{K_{O_2} + \text{O}_2} \quad (5.1)
$$
The same equation was reported also by Sun et al. [110].

To estimate the competitive inhibition effect and the inactivation model, Dixon’s (equation 5.2) and Haldane’s (equation 5.3) equation have been respectively used:

\[
\frac{-dC_1}{dt} = k_1 X \frac{C_1}{K_1 + C_1 + \frac{K_1}{K_2} C_2}
\]

(5.2)

\[
\frac{-dC_1}{dt} = k_1 X \frac{C_1}{K_1 + C_1 + \frac{C_1}{K_I}}
\]

(5.3)

It has been seen that the Dixon’s equation is true for several primary substrates, except for toluene.

**Anaerobic biodegradation of TCE** TCE degradation can also occur under anaerobic conditions. This situation is not so common inside bioreactors for waste air treatment and, if it’s present, it is limited only in the deepest biofilm layer.

Anaerobic and aerobic degradation have shown similar behaviour: both require cometabolites and, therefore, both develop competitive inhibition and present toxic by-products in their pathway. The energy efficiency for the cometabolism results much lower under anaerobic conditions. Kinetic models are mainly the same and only reaction constants change.

The main difference between the two different conditions is that anaerobic biodegradation results more affected by the transition-metal coenzymes, like vitamin B_{12} (Co), which can catalyze the dechlorination process[122].
5.4. TCE Biodegradation

Figure 5.3: TCE degradation pathway for *Methylosinus trichosporium OB3b* [*] and *Burkholderia cepacia G4* [†].
Trichloroethylene (TCE)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{Cl} & \quad \text{H}
\end{align*}
\]

Trichloroethylene

\[
2\text{H}_2\text{O} \quad \text{sMMO} \quad 2\text{H}^+ + 2\text{e}^-
\]

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{Cl} & \quad \text{C} \\
\text{Cl} & \quad \text{H}
\end{align*}
\]

Trichloro-ethandiole

\[
3\text{H}^+ + 2\text{e}^- \quad \text{Dehydrogenase} \quad 2\text{H}^+ + 2\text{e}^- \\
\text{Cl} & \quad \text{C} \\
\text{Cl} & \quad \text{O} \\
\text{Cl} & \quad \text{O}
\]

Trichloroacetate \quad \Leftrightarrow \quad \text{Trichloroethanole}

\[
\begin{align*}
2\text{H}_2\text{O} \quad \text{Haloacid dehalogenase} \quad 2\text{H}_2\text{O} \\
4\text{H}^+ + 3\text{Cl}^- + 2\text{e}^- \quad [\star] \\
\text{CO}_2 & \quad \text{[} \quad \text{Oxalate} \\
\text{O} & \quad \text{C} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\[\text{Oxalate}\]

\[\text{Oxalate}\]

\[\text{Oxalate}\]

Figure 5.4: TCE degradation pathway for \textit{Methylosinus trichosporium OB3b}. [\star] strains PP3 and K5/5; [\natural] strain 113.
5.5 Biofiltration of TCE Vapours

TCE has been treated in all the typical biofiltration equipment. Iranpour et al. [54] reported many studies carried out on bench-scale and in on-site bioreactors to control TCE. Even if both conventional biofilters and biotrickling filters have been used, the latter seems to be a more suitable configuration to degrade this kind of pollutant.

The presence of a moving liquid phase can provide a good mean to reduce the concentration of toxic and acidifying compounds from the fixed-bed. Indeed, it has been seen that some intermediate from TCE degradation pathway can inhibit the enzymatic reaction reducing the removal efficiency.

One problem concerning the use of biotrickling filters is the rapid deactivation of the biomass. To increase the operation time and the process stability, Lee [73] combined a biotrickling filter with a continuous stirred tank reactor, in which biomass could be reactivated. In this condition, the treatment could be prolonged for more than three months without decreasing the removal efficiency.

Some studies [109, 110] also revealed that higher growth rates were achieved near the gas inlet, generating therefore a biomass stratification along the bioreactor.

Other studies [98] reported the utilization of a membrane bioreactor to treat TCE. This bioreactor could achieve a good efficiency, because it seems that both aerobic and anaerobic conditions occur inside it. In anaerobic conditions, TCE is partially dechlorinated and converted in compounds, that can be easily transformed by aerobic biomass. By the way, no experimental evidence confirms the presence of anaerobic conditions.

Bioscrubbers can also be used [124] because they are really suitable to remove acid-byproducts from the bioreactor.

Recently a new bioreactor, called Foamed Emulsion Bioreactor (FEBR), has been used to treat TCE [61, 63]. High efficiency (96% in the first day and 80% after four days) could be achieved. FEBR provides high contact surface between gas and liquid phases and it seems to be more suitable to treat hydrophobic compounds.

The presence of TCE among others volatile pollutants and the effect of this cross-substrate on the biofiltration efficiency have also been studied [29, 118]. In this case, a consortium of microorganisms is normally required to achieve high efficiency for each compound. Moreover, it has been demonstrated that the toxicity of TCE and its by-products is reduced if operating with a mixed culture [29]. Working with consortium will probably increase the stability of the biomass, allowing long-term operation.

A comparison among some studies concerning TCE removal from a vapor phase is represented in table (5.2).
5.6 Other Chlorinated Compounds

Other chlorinated compounds are very common in gaseous effluents. Many studies have investigated the better conditions to reduce their emissions. In his review, Iranpour et al. [54] cited studies concerning the biodegradation of dichloromethane (DCM), perchloroethylene (PCE), monochlorobenzene (mCB), chloroform, trichloroethane, carbon tetrachloride and vinyl chloride (VC). Even if all these are halogenated compounds, their degradation pathway may differ a lot and consequently the optimum condition for the process couldn’t be the same.

Mono-chlorobenzene (m-CB) biodegradability in a biotrickling filter was studied under different concentration, pH, residence time and leachate flow conditions [86]. With high biomass amounts, m-CB showed high removal rate, comparing to benzene and toluene and it doesn’t require a specific cometabolite.

Dichloromethane, as chloromethane, is the only chlorinated hydrocarbon which doesn’t require cometabolites to be aerobically degraded. Best removal efficiencies were obtained using biofilters, rather than biotrickling filters [108].

Vinyl chloride (VC) can be generated by anaerobic biodegradation of TCE. Strains of Pseudomonas sp. can degrade it aerobically, using ethane as growth substrate [113].

Conclusions  TCE has been seen to be a common and hazardous pollutant and it can be present in groundwater, waste gases and soils. Fortunately, it is biodegradable by a specific or unspecific biomass if a suitable carbon source is provided to the microorganisms. To achieve high mineralization efficiency, it is necessary to consider many different aspects, such as primary substrate/TCE rate, toxic by-product formation, temperature, pH, biomass characteristic and the type of bioreactor.
Operating and design assumptions

Trichloroethylene (TCE) was chosen as target pollutant, since it is particularly stiff to be degraded. It was expected that results obtained with such pollutant could be extended to others contaminants.

TCE is poorly soluble and hardly biodegradable; a primary substrate is required for synthesizing TCE-degrading enzymes; its biodegradation pathway generates toxic (TCE-epoxide) and acidifying (Glyoxylic acid) by-products.

Considering all these characteristics and properties, bio trickling filter (BTF) was expected to achieve the best removal efficiency. Also the choice of the carrier is motivated by the specific pollutant under investigation.

The deep knowledge of the waste gas composition is necessary to operate the correct design specifications.

6.1 Target pollutant: Trichloroethylene

Trichloroethylene is a very hazardous VOC generated by several industrial activities. Many studies have employed biotechniques to reduce its emissions. From the study of the literature, it was concluded that TCE degradation is particularly stiff.

First of all, TCE has a very low solubility in water (about 1g/l at 25°C). The amount of pollutant transferred into aqueous phase and available by biomass is therefore limited. Solubility in water is usually correlated to Octanol/water partition coefficient and indirectly to biodegradability. Indeed, it should be noticed that very soluble pollutants (as alcohols) can be more easily biodegraded [36]. Mass transfer rate is thus fundamental to achieve good removal efficiencies.

TCE can be degraded only in the presence of a primary substrate. Waste gases containing other pollutants, as phenol or toluene, can provide the right amount of cometabolites. On the contrary, if working only with TCE in the inlet gas, addition of carbonaceous substrate is required. This addition may be easily carried out introducing some nutrients into the trickling liquid or directly into the biodegradation unit, if working with bioscrubbers.

During TCE degradation, some toxic or acidifying by-products are generated. TCE-epoxide (C₂HCl₃O) reduces the enzymatic activity, while Glyoxylic Acid (C₂H₂O₃) may contribute to reduce the pH. Flushing of toxics and pH control are therefore fundamental in TCE removal.

Strategy To remove TCE, bioreactors should have high specific surface to increase mass transfer, a system to add nutrients for biomass cometabolism, and a system to remove toxics.
from inside the bed and to control pH.

Even if many bioreactors have been applied to treat TCE, biotrickling filter seems to be the most promising. Trickling liquid can be a good mean to control pH, to remove toxics and to introduce the primary substrate for biomass activity.

6.2 Suitable equipment: Biotrickling filter

Biotrickling filters are characterized by a mobile liquid phase which trickles throughout the bed. This trickling liquid is normally recirculated and it provides a good mean for controlling the process.

To avoid bed compaction, inert carriers are usually employed because their higher mechanical resistance. However, inert carrier requires a biomass inoculum, it has lower specific surface area and it has lower buffer and retentive capacities comparing with organic packings. BTFs are very sensible to biomass growth which can reduce the cross sectional area, causing channeling, clogging and reducing reactor performance.

Gas flow is usually down-ward. Co-current operation is often preferred because the amount of pollutant recirculated with the trickling liquid is lower. In despite of the better mass transfer, the risk of gas stripping at the top of the BTF is higher in counter-current operations; thereby, counter-current mode is scarcely employed.

Optimization of BTF design The use of an inert carrier and the lower performance of counter-current operations limit BTF performance.

Working with a mixture of organic and inert carrier, higher efficiencies may be achieved. Organic packings have higher specific surface area, good buffer capacity and good nutrients and moisture retention properties. In this study, compost was selected as the organic media, because, besides having a well-developed biomass, it is particularly suitable in biofiltration processes.

Inert carrier is suitable to reduce the risk of bed compaction and to allow a good air stream distribution across the section area. The most suitable compost/inert carrier ratio has to be determined, in order to avoid bed compaction and bed acidification as well. This can be obtained by some preliminary an empirical analysis of the fluidodynamic behaviour in absence of pollutant.

A simple design modification has been realized to limit all the problems related to the counter-current mode. If trickling liquid is treated before being recirculated, the amount of soluble pollutant fed at top of the reactor may be limited. This treatment can be achieved by a second trickled bed unit, set below the biotrickling filter, which can biologically remove the pollutant from the leachate.

The BTF under investigation was therefore set up with two units: the upper unit operated as a common biotrickling filter with up-ward gas flow; the lower unit treated the TCE which had been solubilized in the leachate. This new design solution allows the feasibility of a counter-current regime, increasing the mass transfer between gas and liquid phase. However, the real requirement of the lower unit has to be still determined.
6.2. Suitable equipment: Biotrickling filter

Conclusions  A new BTF design was conceived to treat TCE vapours. Equipment modification dealt with the introduction of a new degradation unit to treat the leachate, allowing counter-current operations. A mixed compost-inert carrier bed could offer the advantages of both these different packings, reducing the risk of compaction, increasing the specific surface area and introducing an active and well-developed biomass.
Chapter 7

Materials and Methods

TCE degradation was exploited in a biotrickling filter (BTF) with a packing of glass cylinders and compost. Trickling water and gas were fed counter-current mode. Biotrickling filter was chosen because it was supposed to tackle better the problems encountered in TCE removal.

A new reactor section was set to remove TCE from the leachate, in order to reduce the amount of contaminant recirculated at the top of the reactor.

The most important parameters and the troublesome aspects of the process were monitored during more than 6 months continuous running.

TCE inlet concentration was increased day by day to evaluate the reactor performance for different loads and to determine the maximum elimination capacity.

7.1 Bioreactor

The biotrickling filter under analysis was configured as a by two glass cylinders units. Every cylinder was 1 meter high and it was supplied with three sample ports at 12, 32 and 88 cm from the bottom; internal diameter was 9.5 cm, and the overall volume of about 9 liters.

Every cylinder was filled with the same packing. Reactor bed laid on a plastic grid placed at 16 cm from the bottom, so that the lower port could be used as gas inlet.

Gas flow was generated by a membrane pump (KNF, N 022 AN.18), with a nominal flow rate of 15 Nl/min.

Initially, air flow was divided to three streams. The first stream was synthetically contaminated with pollutant and fed to the upper biotrickling filter cylinder. The second stream served to supply oxygen to the lower unit for preserving viable biomass, and the latter was set to avoid pressure stress on the pump. The flow rate of all the three streams were measured by rotameters (FIP) and regulated by valves.

First stream itself was split into two lower streams, whose rate was regulated by two valves and monitored by two rotameters (Dwyer, series RMA): one was fed to a 1 liter gas bubbling bottle (Drechsel type) filled with TCE and the second to an identical bottle filled with water. In this way, it was possible to change pollutant concentration in the inlet flow, without changing the overall flow rate by regulating the flow rates fed to the Drechsel bottles.

The overall gas flow rate coming out from the top of the BTF was measured with a S.I.M. Brun flowmeter. Since rotameters are slightly affected by the downstream pressure drop, the value they revealed may be not completely reliable and a more detailed measurement was thus required. Gas flow rate was daily measured and its values were included between 275 and 285 l/h. Gas flow passing throughout the Drechsel bottles had a rate of about 210 l/h.

61
Water phase was recirculated with a peristaltic pump 323 S/D from Watson-Marlowe, with four roller pumphead, working at 3 rpm with silicone tubing with 4.8 mm internal diameter. Leachate flow rate was constant at about 4.5 ml/min.

At the bottom of the biotrickling filter, a little reservoir of leachate was conceived. Nutrients addition and water make-up were supplied by means of a reservoir bottle with an average volume of 700 ml, parallel to the bioreactor. In this way, the peristaltic pump recirculated a mixed liquid, coming from the BTF and the nutrients vessel respectively.

Moreover, placing the nutrients bottle at the same height of the leachate reservoir in the BTF may be a good mean to determine the pressure drop inside the column, measuring the difference in the level between the two free-surfaces.

A scheme of the plant is represented in figure (7.1).

![Figure 7.1: A scheme of the biotrickling filter used for TCE removal. C: air pump, P, recirculating water pump.](image)

**Packing and bioreactor filling** The packing was a mix of compost and glass hollow cylinders. Many attempts were conducted to assess the best ratio between the two carriers and the most suitable procedure to fill the reactor (see chapter 8). A compost/glass ratio of 1:5 has been seen to grant good fluidodynamic conditions.

500 ml of glass cylinders were first introduced to give a support with good mechanical properties. Then, 5 mixtures, constituted of 200 ml of compost and 900 ml of glass cylinders, were successively introduced. In this way, more homogeneous conditions inside the reactor
7.2 Analysis

7.2.1 COD (Chemical Oxygen Demand)

COD (Chemical Oxygen Demand) is the measurement of the oxygen, that is required for the complete oxidation of the organic substances content of a liquid sample. COD has been widely used to indicate the organic load of a wastewater and it is a fundamental parameter for the conduction of a wastewater treatment plant.

Its value takes into account biodegradable and non-biodegradable substances as well: for this reason, it is not the amount of nutrients exactly. In the specific case of compost, there is a big amount of complete mineralized species, which affect COD measurement but can’t be consumed by microorganisms.

COD was determined by colorimetric analysis. Each sample was introduced in a vial containing some very oxidizing reagents and heated for 2 hours at 150°C. Than, vials were analyzed in a **HACH DR/2010** spectrophotometer which directly displayed COD data expressed in mg/l.

Samples were taken from the middle of the bioreactor, just few centimeters below the inlet of the polluted gas. Trickling water was collected in a cap, which was placed just at the top of the bed of the lower section of the reactor, and sampled by a syringe.

It was supposed that COD value in this position would be more representative of the process. Indeed, sampling from the recirculated liquid could be affected by some flow rate fluctuation.

7.2.2 Gas chromatography

TCE concentration in both liquid and gas flows was measured by means of a Gas Chromatograph (GC) **DANI GC 1000 DPC**, equipped with two **Electrons Capture Detectors** (ECD). GC had two analytical lines, each one with an automatic autosampler **DANI VU65** and a capillary column **Poraplot U** (length=10 m, internal diameter=0.32mm). Every line operated at the same conditions.

Helium was employed as carrier gas and nitrogen as auxiliary gas to pilot the autosamplers and to flush the detectors.

Injection system was a split-splitless injector **SL/IN 86/2**. Split rate was changed from 10 to 30, in order to flush to the detector a TCE concentration below the limit of linearity between the signal of the detector and the concentration.

Analytical conditions are reported in table (7.1). Auxiliary gas pressure was set to have a flow rate of 35 ml/min flushing the detector.
7. Materials and Methods

<table>
<thead>
<tr>
<th>Analytical conditions</th>
<th>GC/ECD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven temperature</td>
<td>170°C</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Gas flow</td>
<td>10 ml/min</td>
</tr>
<tr>
<td>Injection gas valve split</td>
<td>10 : 20</td>
</tr>
<tr>
<td>Auxiliary gas pressure</td>
<td>0.95 bar</td>
</tr>
</tbody>
</table>

Table 7.1: Analytical condition for TCE analysis in DANI GC 1000.

Autosamplers had a sampling loop of 250 µl and they were employed to measure TCE concentration in the inlet and the outlet flow. Autosamplers were directly connected to the biotrickling filter by HDPE tubing, with a flow rate of about 5 ml/min.

TCE concentration in the gas flow was monitored two times a day, in the early morning and in the evening. TCE concentration data were obtained as the average value of three subsequent measurements.

TCE concentration in the leachate was measured by GC/ECD analysis as well. Static head space method was used, employing the same procedure reported by APAT, IRSA-CNR [130]. Sample volumes of 5 ml of leachate were collected and stored in a 10 ml vial, hermetically closed by a silicon-PTFE cap and aluminium crimp. Vials were heated for 20 minutes at 80°C and than 250 µl of the vial head space were collected by a gas syringe and injected into the GC.

Liquid samples were collected from the middle of the column, just few centimeters below the gas inlet, and from the bottom of the reactor, in order to evaluate the effectiveness of the lower BTF unit in the removal of TCE from the leachate. This analysis was usually conducted two times a week; more frequent measurements were performed if necessary for the specific experiment requested it.

Calibration curves Calibration curves were obtained using well-defined TCE concentration in organic solvent. Normal Heptane (n-C7) was used since its low volatility and high TCE solubility. Moreover, n-C7 can not be detected by ECD detector and it doesn’t reduce the life of the column packing. Injection volume was set to 1 µl. Concentration were expressed in volumetric rate [µl/l] (figure (7.2)).

For the liquid phase analysis, a calibration procedure was carried out using TCE/water solutions at known concentration, and using APAT, IRSA-CNR [130] method as well.

7.2.3 Other Analysis
Pressure drop, pH, TS and VSS amount in the leachate and trickling water flow rate have been measured.

Pressure drop was determined by a hydrostatic U-shaped manometer filled with water. Pressure drop measurements referred to the whole packing, between the bottom of the lower unit and the atmospheric pressure.
7.3. Nutrients

Compost itself has a great amount of nutrients, especially micronutrients like Fe, Cl, Cu. However, carbonaceous and nitrogenous substances are readily consumed by biomass and new addition is required.

A simple nutrients solution was prepared with Sodium Acetate (CH$_3$COONa) and Sodium Nitrate (NaNO$_3$). All the other nutrients, including phosphorus, were supposed to be already present in the leachate. Sodium Acetate was chosen as cometabolite for TCE degradation since it has alkaline properties.

Nutrients solution were composed of 20 g/l of CH$_3$COONa (BOD$\approx$COD=17.55 g/l) and 10 g/l of NaNO$_3$ (1.64 g N-NO$_3$) (BOD:N=100:9.34). The typical ratio between carbon and nitrogen (BOD:N=100:5) [81] was not respected, since it was supposed that the carbon from TCE degradation could contribute to the microorganisms demand. Moreover, higher acetate concentration could develop some competitive effects, reducing TCE removal efficiency.

Ten milliliters of nutrients solution were daily introduced into the nutrients bottle (see figure 7.1). Supposing that the peristaltic pump displaced at the same time the same volume from the bottom of the biotrickling filter and the nutrients bottle, fresh nutrients...
concentration in the recycling water can be fixed at about 120 mgCOD/l and 11 mgN-NO_3/l.

7.4 Biotrickling filter piloting

The Biotrickling filter continuously operated for more than 6 months.

- First month was employed to assess the fluidodynamic stability of the pilot plant. Pressure drop and leachate flow rate were monitored without TCE. Nutrients were added to the system to maintain biomass activity and to acclimate it to the new conditions.

- After this period, a gas stream containing very low TCE concentrations was fed to the system 2 months along. In this way, a suitable biomass for the removal of TCE was selected.

- Finally, TCE concentration was increased, in order to evaluate the maximum elimination capacity and the bioreactor performance. This increase in TCE concentration was then stopped because technical and practical problems: the response of the system was too slow and an excessive amount of TCE was necessary to evaluate the efficiency at steady-state conditions. During this period, the following parameters were daily monitored: TCE concentration in the gas flows and in the leachate, liquid and gas flow rates, pressure drop, leachate pH and COD.

- Subsequently, a simple experiment was carried out for the evaluation of the transient behaviour of the pilot-plant: a sudden addition of TCE was provided to the system and pollutant concentration in the inlet and in the outlet were continuously monitored to check the response of the system.

- A further study was performed to evaluate the effects of gas and leachate flow rates on the biotrickling filter performance. Experiment was carried out approximately with the same inlet concentration and pH, pressure drop and TCE concentration in the leachate were daily measured.

7.5 Calculations

Biotrickling filter performance is usually evaluated considering the elimination capacity, the inlet load and the removal efficiency, which are defined as follows:

\[
L = \frac{C_{g,in}QV}{V} \tag{7.1}
\]

\[
EC = \frac{(C_{g,in} - C_{g,out})QV}{V} \tag{7.2}
\]

\[
RE = \frac{C_{g,in} - C_{g,out}}{C_{g,in}} \cdot 100 \tag{7.3}
\]

In the pilot-plant here described, only the upper unit operated as a BTF, while the lower column served to remove TCE from the liquid phase. Therefore, the determination of the performance parameters could be not so easy.
In figure (7.3), an outline of the flows involved in the process and the corresponding concentrations is reported. Supposing $C_{g,2} \approx 0$, all the values were experimentally evaluated, apart $C^*_{g,2}$ which is the concentration in the gas flow coming from the lower unit. This is fundamental to determine the $C_{g,in}$ and, thereby, $EC$ and $RE$.

Two limit conditions for the lower unit can be set.

If only reaction occurred, no pollutant was transferred into the gas phase and, therefore, $C_{g,2} = 0$. A TCE mass balance around the dashed line of figure (7.3) permits the calculation of $C_{g,in}$:

$$C_{g,in} = \frac{G_1 C_{g,1}}{G_1 + G_2} \quad (7.4)$$

In this condition, the overall removal efficiency and the elimination capacity of the BTF section was reduced, since part of the TCE was degraded by the lower unit.

On the contrary, supposing that stripping only occurred, $C^*_{g,2} > 0$ and it could be calculated from the mass balance around the lower unit:

$$C^*_{g,2} = \frac{Q_L (C_{L,in} - C_{L,out})}{G_2} \quad (7.5)$$

and $C_{g,in}$ resulted:

$$C_{g,in} = \frac{G_1 C_{g,1} + G_2 C^*_{g,2}}{G_1 + G_2} \quad (7.6)$$

In this case, BTF operated the whole degradation of TCE, and $RE$ and $EC$ have their maximum values.

---

1 Absorption in the space between the two beds is supposed negligible.
Presumably, both reaction and desorption occurred in the lower unit, so far that the real value of $C_{g,2}^*$ is included between 0 and the value obtained from equation (7.5).

However, for any further calculation, gas stream coming out from the lower unit bed was supposed to have a negligible TCE concentration. This assumption can be validated by the fact that the rate between $Q_L$ and $G_2$ in equation (7.5) has, in fact, a really very low value (0.0038 with $Q_L=4.5\text{ml/min}$ and $G_2=70\text{l/h}$), so far that $C_{g,2}^*$ can not have strong effects on the value of $C_{g,in}$.

$L$, $EC$ and $RE$ were hence calculated using $C_{g,in}$ from equation (7.4), with $Q_V=G_1+G_2$ and $V$ the volume of the upper unit alone.

With the same assumption, the removal efficiency of the lower unit of the pilot plant can be calculated:

$$RE_l = \frac{C_{l,in} - C_{l,out}}{C_{l,in}} \cdot 100$$ (7.7)

not considering if such efficiency is attributable to a biodegradation or to any stripping effects.

**Conclusions**  A pilot-scale BTF was here realized and equipped with all the units necessary for its operating and control. BTF was characterized by a section to treat the leachate and by a mixture of compost and inert carriers as packing. TCE measurement was achieved with a GC/ECD in order to assess BTF performance. Pressure drop and pH were also controlled, since they are responsible of the most common and frequent malfunctioning. $L$, $EC$ and $RE$ of the BTF were calculated supposing that in the lower unit only bioreaction occurs. It has to be remarked that the choice of the most suitable equipments to be used in the development of the present work had played an essential role during PhD activity. Furthermore, a particular pilot-plant was designed and built-up in order to examine different parameters action on TCE biological removal.
Preliminary studies were carried out to evaluate the best configuration of the packed bed. A mix of compost and inert glass cylinders was used, but their ratio could strongly affect the fluidodynamic conditions. An excessive compost amount could cause bed compaction, an increase of pressure drop and a reduction of the performance. On the other hand, compost amount should be sufficient to assure pH control and to provide an adequate biomass content. Some different compost/inert ratios were tested and also another inert carrier was employed. The procedure to execute the filling of the reactor was taken into consideration as well, in order to have homogeneous conditions inside the bed. The operability of the packed bed was investigated during some weeks in order to assess its suitability. Finally a compost/glass cylinders ratio of 1:5 was stated to allow good performances, without affecting the fluidodynamic behaviour of the bioreactor.

8.1 Operating procedure

A preparatory run was carried out using the pilot-scale BTF previously described, with a gas flow rate of about 300 m$^3$/h and a trickling water rate of 7.5 ml/min. A nutrient solution was continuously fed to the system in order to preserve microbial activity and to promote biomass growth. Compost came from a MSW composting plant (its properties have been already described).

The fluidodynamic behaviour was evaluated considering some empirical results:

**Biomass distribution** During operation, the growth of the biomass is so evident that it can be seen naked-eye. The presence of microorganisms along the bioreactor height and even across the sectional area is a good mean to evaluate the gas and trickling water distribution. Indeed, biomass needs both nutrients and oxygen for its metabolism. Moreover, an excessive amount of fungi (which are characterized by iphae, typical of molds) could be a critical sign of starvation conditions: in fact, fungi can better face nutrients or oxygen lack, comparing with bacteria.

**Bed compaction** Bed compaction can particularly occur with organic matter. It can generate retention of trickling liquid inside the reactor and flooding condition may become a serious risk.

**Channeling** Because the bed compaction, liquid flow preferably passes throughout the regions with a higher cross sectional empty area. Bed compaction can increase this phenomenon,
which is more evident along the bioreactor walls. In such conditions, the inner regions of the biotrickling filter are not reached by nutrients and water.

**Biological Foam** If stressed, microorganisms can generate a biological foam, that can be carried at the top of the reactor by gas flow: it is a visible sign of malfunctioning.

**Biomass deactivation** By a respirometric analysis of the trickling water, it is possible to evaluate the activity of the suspended biomass and, approximately, of the biofilm. Under malfunctioning conditions, this activity should be strongly reduced.

**Test #1: compost/inert = 1:1, with alternated layers**

The first test was carried out using a compost/glass cylinders ratio of 1:1 and introducing in sequence and alternatively 500 milliliters of organic and 500 milliliters of inert carrier. The first layer was constituted by glass cylinders to achieve a better gas distribution. Trickled bed had a final volume of about 5.5 liters, introducing 3 liters of compost and 3 liters of glass cylinders. The reduction in the overall volume was due to the fact that compost partially covered the void volume of the layer filled with inert carrier.

The test run lasted two weeks. A moderate build-up of trickling water and biological foam was observed at the top of the bed. Molds grew along the whole reactor, especially onto the bioreactor walls. Also channelling mainly occurred along the BTF wall, being mainly present in the compost layers.

The filling procedure was supposed to be not effective, since malfunctioning was especially observed along the compost layers.

**Test #2: compost/inert = 1:1, with homogeneous layers**

To overcome the limits encountered in test #1, a new filling procedure was considered introducing 6 liters of a mixture of compost and inert carriers, with the same volumetric ratio.

Anyway, bed compaction was still observed along the whole column. Pressure drop was even higher than the one measured in the previous test. Channeling onto the bioreactor walls was present the entire height along with formation of large gas bubbles. The compost amount was considered to be too high for a good fluidodynamic behaviour.

Respirometry was carried out using the leachate from the BTF after two weeks of operation and no biological activity was observed. Respirometric data were compared with other experiments carried out with a leachate from a compost sample having the same origin and age.

By emptying the reactor, it was noticed that molds were prevailing onto the walls, indicating bad gas and liquid flow distribution.

**Test #3: compost/inert = 2:5, with homogeneous layers**

In this test, a lower compost/inert carrier ratio (2:5) was used. Moreover, glass cylinders were substituted with some polyethylene rings (diameter=24 mm, height=10 mm, density=900 Kg/m³, specif surface area=500 m²/m³), also employed in Moving Bed Biofilm Reactor (MBBR) for waste water treatment. 500 milliliters of inert carrier were first introduced into the bioreactor; then, 4 layers of 1125 milliliters of inert and 500 milliliters of compost were added, for an overall bed volume of 6 liters.
The same problems encountered in the previous tests were here obtained. The new packing seemed to be not suitable to avoid bed compaction and flooding even if compost amount was much lower.

Figure (8.1) illustrated the working condition during test #3. Since its low density, carrier is lifted up by gas bubbles.

![Figure 8.1: Example of flooding as consequence of an excessive bed compaction. Results obtained using 2:5 compost/inert carrier.](image)

**Test #4: compost/inert = 1:5, with homogeneous layers**

The latter test was finally successful. Bed was constituted by a layer of 500 milliliters of glass cylinders and 5 subsequent layers of a mixture with 900 milliliters of inert carrier and 200 milliliters of compost.

No channeling was observed along the reactor walls, not even liquid build-up at the top of the bed. Biomass seemed to be locate not only around the package, but inside the bed as well.

After some weeks of stable operation, liquid flow rate was increased to 70 ml/min in order to evaluate the onset of flooding conditions. The system operated without excessive pressure drop or channeling. During the whole experiment, no biological foam was noticed.

By using the new compost/inert ratio, good fluidodynamic conditions were achieved: however, it should be evaluated if the quantity of native compost biomass is enough to allow sufficient removal efficiencies.

**Conclusions**  
A preliminary analysis was carried out in order to establish the best compost/inert ratio for the BTF operation. The choice was performed with the empirical analysis of flooding, channeling, foaming, and biological growth. The optimum gas and liquid flow distribution is fundamental to increase the removal efficiency, since sufficient amounts of oxygen, pollutant and nutrients for biomass growth and maintaining must be present in the whole bed.
Chapter 9

Results and discussion

The pilot-scale biotrickling filter continuously operated for more than 6 months; TCE was provided to the system 30 days after its start-up. The day of the first TCE addition was set as day-zero and all the results were related to this date. The first period of operation was employed to evaluate the maximum elimination capacity ($EC_{\text{max}}$): TCE concentration in the inlet gas flow was increased at constant gas and leachate flow rates. An average removal efficiency of about 75% (with a minimum of about 50%) was achieved, and an $EC_{\text{max}}$ of 5.61 g/(m$^3$·h) was obtained.

Experimental data of $E_C$ and $L$ were fitted by using the Ottengraf-modified model, whose employment was limited by the impossibility to obtain data from the reaction limitation area.

Afterwards, the course of the removal efficiency for different gas and leachate flow rates was investigated. This study was performed from day 136 until the end of the operations. As a result, $RE$ showed to increase as leachate flow increases and gas flow decreases.

A simple test was also carried out to evaluate the response time of the pilot-plant when a positive TCE concentration step was applied. Leachate, pH and pressure drop were monitored daily during the whole operating period and strong variations of their values were not noticed.

9.1 Results from the BTF piloting

Many process parameters had been measured during the whole experiment, including TCE concentration in the gas flow inlet and outlet, the pressure drop along the whole reactor and the pH of the leachate.

Figure 9.1 reports gas and liquid flow rates measured during the experiment. In the test carried out to assess $EC_{\text{max}}$, $Q_L$ and $Q_V$ remained mainly constant, with an average flow rate of 4.49 ml/min and 281.6 l/h respectively.

Slight fluctuations of $Q_V$ values were mainly due to changes in pressure and in temperature.

After day 136, $Q_V$ was reduced to 114.9 l/h, while $Q_L$ was increased twice: the first time from 4.49 to 33.2 ml/min and the second time to 49.5 ml/min.
9. Results and discussion

9.1.1 TCE concentration and removal efficiency

Removal efficiency course during the operating period is represented in figure (9.2). In this figure, TCE concentration and the emission limit are reported as well.

During the first 60 days, TCE concentration in the inlet gas was maintained at very low values, in order to allow biomass acclimatization towards the pollutant. $RE$ values remained mainly constant at about 80%. It should be noticed that the total TCE degradation had never been achieved even at low inlet concentrations. This could be due to an incomplete acclimatization or to a sensible limitation in mass transfer. According to the last assumption, it can be stated that the contact surface area and the operating conditions could not be suitable for the complete TCE absorption.

After day 60, TCE concentration was readily increased to a maximum value of 0.1921 g/m$^3$ with a corresponding $RE$ of 63.4%.

Further increases were not possible because some practical problems. Indeed, long periods were required to reach the stationary condition in order to obtain reliable data and TCE consumption during these periods were excessive. Moreover, emissions from the bioreactor were already above the limit fixed by the regulation and any further addition was not possible.

The great fluctuation of the TCE concentration (especially in the inlet flow) was likely determined by some little changes in the gas flow rate, in the pressure drop, and in some variation in the pollutant level inside the Drechsel bottle.

TCE concentration in the outflow began to exceed the emissions limit at an inlet concentration of about 0.07 g/m$^3$. In these conditions, the removal efficiency was about 60%.

The vertical dashed line detects the start of the operating conditions, when gas and leachate flow rates were changed. For this new test, TCE inlet concentration was set in order to obtain a waste gas with a pollutant amount higher than the emission limit (about 0.04 g/m$^3$). It can be seen that $RE$ increased even at constant inlet concentrations, stating that the new operating conditions enhanced the bioreactor performance.

---

1 Limit fixed by d.lgs 152/2006, attachment III of part V.
9.1. Results from the BTF piloting

Figure 9.2: TCE concentration in the inlet and in the outlet flow and the corresponding removal efficiency during the whole experiment. The vertical dashed line separates the test carried out in order to determine the maximum elimination capacity from the test for the evaluation of the system response to different gas and leachate flows.

9.1.2 Pressure drop and pH of the leachate

As previously discussed, pH variation and pressure drop are two of the main problems causing biofilter and biotrickling filter malfunctioning. Bed acidification is more considerable when chlorinated compounds, as TCE, are present. Moreover, bed compaction due to an excessive moisture level or biomass growth can reduce the performance of a biofiltration process.

Figure 9.3 shows the time course of pH and pressure drop during the whole experiment.

Pressure drop remained mainly constant at an average value of 3 cmH₂O. It was observed that Δp fluctuations were mainly due to a gradual fouling of the tubing from the reservoir bottle to the peristaltic pump, rather than to bed compaction.

Also pH values remained stable at an average value of 10.02 during the whole experiment. It should be remarked that bioreactor operated in alkaline conditions. This is a not common situation in biofiltration process [67] since microorganism are supposed to work better at about 7 [83]. Moreover, the degradation of compost biodegradable substances did not produce any acidification of the bed.

Alkaline conditions likely occurred because of compost buffer properties and because of the addition of sodium acetate as nutrient.

However, it should be noted that pH remained constant: compost buffer properties likely prevailed over TCE acidifying by-products.
9. Results and discussion

The use of the mixture compost/glass cylinder was successful: inert packing avoided bed compaction and compost allowed a good pH control.

The same results were obtained also with different liquid and gas flow rates. Pressure drop is affected by moisture level, since an excessive recirculation may reduce the cross sectional area, causing clogging and flooding. However, the new operating conditions did not affect these two important process parameters.

![Figure 9.3](image)  
*Figure 9.3:* Pressure drop along the whole column and pH of the leachate during the whole experiment vs. time. The vertical dashed line separates the test carried out in order to determine the maximum elimination capacity from the test for the evaluation of the system response to different gas and leachate flows.

9.1.3 TCE removal from the leachate

To evaluate the relevance of the lower unit of the pilot-plant, TCE concentration in the leachate was measured at the top and at the bottom of this section. Figure 9.4 shows concentration data and removal efficiency $RE$ referred to the lower unit.

Removal efficiency had been higher than 95% during the whole experiment, even with different gas and leachate flow rates. This fact is due to both biological oxidation and gas stripping. The increase in TCE concentration matches with the amount of pollutant in the waste gas, so that the peak in TCE$_{mid}$ corresponds to the peak in TCE$_{in}$ of figure 9.2.

Starting from this high $RE_t$ value, it can be stated that the amount of TCE recirculated at the top of the column is much lower than the one which could be obtained without the lower unit. The new BTF design proposed was thus successful, because it enhanced the performance of the whole process carried out in counter-current mode.

However, since the leachate flow rate is much lower than gas flow rate, the contribution of the recirculated pollutant on the BTF removal efficiency is negligible. Indeed, by a simple mass balance around the top of the BTF and supposing that the whole pollutant is immediately transferred into the gas phase by stripping, the additional TCE concentration is equal to $Q_L/Q_V \cdot$TCE$_{bott}$. Assuming average values for the flow rates ($Q_L = 4.49$ ml/min and $Q_V$.
9.1. Results from the BTF piloting

= 281.6 l/h) from the first part of the experiment, the maximum increase in the gas outlet concentration was $2.8 \times 10^{-5}$ g/m$^3$, about the 0.3% of the overall TCE outlet concentration.

By varying liquid and gas flow rates, it was possible to increase the TCE amount that passed into the water phase. In figure (9.4), after the vertical dashed line, a strong increase in $TCE_{mid}$ was observed, even if pollutant concentration in the inlet gas flow was basically constant (see figure (9.2)). In spite of this increase, $RE_l$ was still over 95%. This condition was achieved by reducing $Q_V$ and increasing $Q_L$.

By these experimental results, it is possible to state that the lower unit operates properly only with an adequate $Q_L/Q_V$ ratio. The effect of different gas and liquid flow rates is investigated in detail in paragraph 9.3.

However, the choice of a low leachate flow rate was justified by the fact that the risk of bed compaction is moderate.

Figure 9.4: TCE concentration in the leachate at the top and the bottom of the lower BTF unit, and the corresponding removal efficiency vs. time. The vertical dashed line separates the test carried out in order to determine the maximum elimination capacity and the test for the evaluation of the system response to different gas and leachate flows.

9.1.4 COD of the leachate

To control biomass activity, the COD of the leachate was also measured. It was supposed that the variation of its value allowed the calculation of the amount of nutrients degraded by the microorganism. Hence, this measurement could be useful to evaluate if biomass requires additional nutrients supply for example.

COD measurement was unfortunately not successful. The contribution of nutrients to the overall COD could not be evaluated because of the great amount of non-biodegradable COD coming from the compost. Figure (9.5) reports COD values measured during the test and also before TCE addition.

As it can be observed from the graph, the measured COD (average value about 26000 mg/l) was really much higher, comparing with the COD of the nutrient solution (120 mg/l).
The great variations in COD values was likely generated by some variations in the moisture level inside the bioreactor, which are mainly due to water stripping, and different leachate accumulation at the bottom of the bioreactor.

COD measurements were concluded after 120 days from TCE addition. The data obtained were not useful to evaluate biotrickling filter performance or to derive some important hints for the bioreactor piloting.

Respirometry could be employed to fractionate the overall COD of the leachate into a rb-COD fraction from nutrients and a nbCOD fraction from compost. However, to obtain reliable data, a great volume of leachate is required and the equilibrium of the biofiltration system could be compromised. Moreover, suspended biomass could strongly differ from attached biomass and kinetic behaviour could be completely different.

However, it should be noticed, that COD measurement could be useful if working only with an inert packing only.

9.2 Evaluation of $EC_{max}$

TCE concentration data were combined with the measurement of the gas flow rate and of the bed volume, in order to obtain the course of the elimination capacity as function of the mass loading rate. Data are reported in figure (9.6) and refer only to the period between days 0-136.

It can be observed that 100% removal efficiency was obtained only in few cases, even at low inlet loads.

EC is proportional to the mass loading rate along the whole analytical range. This means that the reaction limitation area was not obtained during the experiment, since in this region $EC$ is constant and does not depend on $L$. The critical value $L^*$ referring to the transition between diffusion and reaction limitation areas is hence higher then the maximum mass loading.
rate obtained in the experiment. In the same manner, $EC_{\text{max}}$ is not equal to $EC_{\text{rl}}$ related to the reaction limitation, since this condition was not achieved.

However, a maximum elimination capacity of 5.61 g/(m$^3$h) was obtained at a mass loading rate of 8.86 g/(m$^3$h).

As it was previously reported, higher pollutant loads were not possible, since TCE consumption was excessive. Increasing gas flow rate would achieve the same effect and, therefore, it was not performed. Higher loads could be obtained also by reducing bed volume, but this possibility has practical difficulties, of course.

### 9.3 Effects of gas and liquid flow rates on BTF performance

After day 136, TCE inlet concentration remained basically constant, and bioreactor performance was investigated using different gas and liquid flow rates.

Figure 9.6 shows the effects of gas flow on the removal efficiency. $EBRT$ data were calculated using the average gas flow rate (275.2 and 114.1 l/h).

As was expected, $RE$ increased with higher $EBRT$ values. Biomass had a longer time to operate the degradation and the increased contact time promoted the mass transfer between gas and liquid phases.

Effects of $Q_L$ are of greater interest. As previously mentioned, higher $RE$ were obtained
at higher leachate flow rates. Increasing $Q_L$ means also an increase of the TCE mass flux fed to the lower unit, which is able to degrade completely this higher amount. It also means that, during the first 136 days, the lower unit operated much below its maximum capability.

By varying $Q_L$, the fraction of TCE degraded by each BTF unit can be changed. Higher liquid flow rates involve a faster TCE displacement from the upper to the lower unit by simple liquid advection. In these conditions, microorganisms from the lower unit can better contribute to the overall TCE biodegradation, with the subsequent increase in the bioreactor performance.

In particular, it was obtained that, with $EBRT=78.5$ sec, $RE$ passed from 67% at 4.57 ml/min to 80% at 33.3 ml/min, while with $EBRT=189.3$ sec, $RE$ passed from 73% at 4.87 ml/min to 87% at 33.32 ml/min.

Figure (9.8) reports TCE$_{mid}$, TCE$_{bott}$ and the removal efficiency related to the lower unit as a function of $Q_L/Q_V$ ratio.

TCE$_{mid}$ passed from 0.0016 to 0.012 g/m$^3$ (7.5 times higher) with a slight reduction of the RE$_l$ value (from 98% to 94%): it means that the lower unit can operate even with higher TCE concentrations.

The choice of the optimal $Q_L/Q_V$ ratio is fundamental to improve the performance of such bioreactor design. Gas flow rate is usually not changeable, since waste gas comes out from a former facility. On the contrary, recycle flow rate can be an useful parameter for biotrickling filter optimization.

$Q_L$ should be selected in order to obtain the maximum TCE removal in the lower unit and a sufficiently low additional TCE concentration at the top of the BTF by recirculation. Moreover, as $Q_L$ increases, the lower BTF unit plays a great role, since the amount of TCE transferred into the liquid phase and recycled to the top of the bioreactor is higher.

Anyway, an excessive trickling liquid flow rate has to be avoided since clogging and flooding could be promoted in such condition. In the present experiment, no malfunction was noted, since pressure drop along the whole bioreactor remained basically constant (see figure (9.3))
9.4 Transient behaviour

A simple test was also carried out to evaluate the response time of the pilot-plant to a sudden step increase of the TCE concentration in the inlet gas flow. Figure (9.9) shows the time course of TCE concentration in the inlet and in the outlet flow. Data were obtained with $Q_V=280\text{ l/h}$ and $Q_L=4.57\text{ ml/min}$.

TCE concentration in the inlet instantly passed from 0 to 0.035 g/m$^3$ at time 0. The measured concentration in the inlet showed 1.5 hours of delay because the time required to pass along the whole tubing connecting the sample port to the gas chromatograph.

It can be observed that the steady-state condition was obtained after about 5 hours. At that time, TCE concentration in the outlet flow was about 0.012 g/m$^3$, obtaining 66% $RE$.

9.5 Biomass growth

Compost had native biomass and no further inoculum was required. Such biomass was demonstrated to be suitable to treat TCE after the selected acclimatization period.

Microorganisms growth was observed during experiment. Many colonies were generated along the entire bioreactor, especially in the low part of the bed of both units. The higher amount of oxygen in these regions likely promoted biomass growth. However, microbial growth was not sufficient to affect the BTF pressure drop.

Some measurements were carried out in order to determine the VSS inside the leachate and to evaluate the presence of some suspended bacteria into the trickled liquid. VSS passed
from 2.24 gVSS/l 20 days before TCE addition to 1.15 gVSS/l at day 140. Thus, the operating conditions partially promoted attached biomass.

### 9.6 Data fitting

Experimental data were fitted by using the Ottengraf’s modified model, discussed in chapter [4]. This model is based relates the elimination capacity and the mass loading rate by the following equation:

\[
EC = A_s k_0 \delta + \frac{L \left( 1 - \left( 1 - A_s \sqrt{\frac{k_0 D}{2m \sqrt{VQL}}} \right)^2 \right) - A_s k_0 \delta}{1 + \left( \frac{L}{L^*} \right)^p} \tag{9.1}
\]

and the calculation of the removal efficiency can be easily obtained by using the definitions of \( EC \) and \( L \):

\[
RE = \frac{C_{g,in} - C_{g,out}}{C_{g,in}} \cdot 100 = \frac{EC}{L} \cdot 100 \tag{9.2}
\]

\( EC \) and \( L \) data used for data fitting were the ones obtained during the test to assess \( EC_{max} \). Fixed and calculated parameters are reported in table (9.1).

The value of \( L^* \) for the initial set was determined by using the definition of the critical Thiele module as referred by Ottengraf [89]:

\[
\phi_{cr} = \delta \sqrt{\frac{k_0 m}{DC^*}} = \sqrt{2} \tag{9.3}
\]
9.6. Data fitting

### Table 9.1:
List of parameters used in the Ottengraf’s modified model. Initial set and calculated set are reported for the fitted parameters. [†]: data obtained using equation (9.4) with the first attempt set of parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Values</th>
<th>Unit</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial set</td>
<td>Final set</td>
<td></td>
</tr>
<tr>
<td><strong>Fixed parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>$Q$</td>
<td>0.2816</td>
<td>m$^3$/h</td>
<td></td>
</tr>
<tr>
<td>Bed volume</td>
<td>$V$</td>
<td>0.006</td>
<td>m$^3$</td>
<td></td>
</tr>
<tr>
<td>Air/water partition coefficient</td>
<td>$m$</td>
<td>0.4</td>
<td>g/g</td>
<td>[44]</td>
</tr>
<tr>
<td>Diffusivity in water</td>
<td>$D$</td>
<td>3.75×10$^{-3}$</td>
<td>m$^2$/h</td>
<td>[99]</td>
</tr>
<tr>
<td><strong>Fitted parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td>$A_s$</td>
<td>1000</td>
<td>999.496</td>
<td>m$^2$/m$^3$</td>
</tr>
<tr>
<td>Biofilm thickness</td>
<td>$\delta$</td>
<td>0.001</td>
<td>0.0161426</td>
<td>m</td>
</tr>
<tr>
<td>Zero-order kinetic constant</td>
<td>$k_0$</td>
<td>10</td>
<td>1.21367</td>
<td>g/(m$^3$.h)</td>
</tr>
<tr>
<td>Critical mass loading rate</td>
<td>$L^*$</td>
<td>25.03[†]</td>
<td>19.9813</td>
<td>g/(m$^3$.h)</td>
</tr>
<tr>
<td>Exponent</td>
<td>$p$</td>
<td>1</td>
<td>1.64808</td>
<td>-</td>
</tr>
</tbody>
</table>

Indeed, as previously described, the transition between the reaction and the diffusion limitation area occurs at $\phi = \phi_{cr}$ or at $C_{g,in} = C^*$.

Using the definition of mass loading rate, $L^*$ can be thus expressed as follows:

$$L^* = \frac{C^* Q}{V} = \frac{\delta^2 k_0 m Q}{2D V}$$  \hspace{1cm} (9.4)

Fitting was carried out using the Levenberg-Marquardt algorithm with $EC$ vs. $L$ data. A coefficient of determination, $R^2$, of 0.921 was obtained by fitting, with a total sum of squares of 1.506 and a residual sum of squares of 0.119.

The final parameters set was successively used to calculate the dependence of the removal efficiency on the mass loading rate.

Figures (9.10) and (9.11) report the experimental data and the model fitting for respectively $EC$ and $RE$ vs. the mass loading rate respectively.

$EC$ vs $L$ plot shows a good agreement between experimental and calculated data. However, the asymptotic profile at very high loads cannot be identified: that is mainly due to a lack of experimental data in this region.

It should be remarked that, even if data from reaction limitation area have not been obtained, model could fit with success.

Biofilm thickness represented the main problem encountered: indeed, the value calculated by fitting (about 0.01 m) is too high, with no physical correspondence with the biofilm/water phase observed during BTF piloting. This anomaly can be explained considering that parameter $\delta$ influences in the model only when the reaction limitation term is considered, and no experimental data were available for this condition.

In accordance with the model, the transition between diffusion and reaction limitation area occurs at 19.98 g/(m$^3$.h), far from the experimental range.
9. Results and discussion

Figure 9.10: Experimental data and model prediction of the elimination capacity and the mass loading rate. The little plot shows data in a smaller load range.

Figure 9.11: Experimental data and model prediction of the removal efficiency and the mass loading rate. The little plot shows data in a smaller load range.
A, obtained by fitting does not strongly differ from the initial value (999.496 to 1000 m²/m³). This fact can be likely due to a weak dependence of EC from the specific surface area, to the specific algorithm used in calculations or, again, to a lack in the experimental data.

Conversely, RE profile is more unstable. This is essentially due to the fact that the limit of RE for \( L \rightarrow 0 \) is equal to \(-\infty\). It means that, for load values close to zero, RE curve suddenly passes from about 100% to \(-\infty\). This behaviour can be observed in the little plot on graph (9.11).

Moreover, in a certain load range, removal efficiency has values higher than 100%. This problem was already encountered during sensitivity analysis and it is due to a stronger contribute of \( EC_{rl} \) in respect to \( EC_{dl} \). The value of parameter \( p \) could be a value mean to reduce this deficiency.

Finally, the slight increase of RE at loading values between 3 and 8 g/(m³·h) has not a physical reason as well: it is supposed that the lack in experimental data from reaction limitation area should be responsible of this behaviour.

In spite of all the limits encountered and discussed, the new model has a good agreement with the experimental data. No comparison with the original Ottengraf’s model was carried out, since the presence of two new parameters surely increased the goodness of fit.

9.7 Discussion

Trichloroethylene removal was successfully exploited in the actual new biotrickling filter design. BTF operated for longer than 6 months and no malfunctioning had been observed during the whole experiment: this fact was mainly due to the choice of the packing material. Mixtures of different carriers are not common in biofiltration processes and they are reported in the literature only for conventional biofilters [39, 100]. Nevertheless, by the simultaneous use of inert and organic carriers, advantages from both carriers can be obtained.

Inert packings have good mechanical properties, but they require a continuous supply of nutrients and alkali for biomass nourishment and pH control. On the contrary, organic carrier has good retention properties but it can easily give rise to bed compaction.

During the experiment, pressure drop along the entire bioreactor remained quite constant: glass cylinders likely provided a good mechanical support to avoid bed compaction. Moreover, in spite of the great amount of TCE removed, pH of the leachate was also constant. This result can be explained with the buffer properties of the compost. However, a little contribute to pH stability should be assigned to sodium acetate as well.

Mass transfer of TCE was really very important, because its low water solubility. This statement can be easily confirmed by elimination capacity data, because, in spite of the great TCE amount in the inlet waste gas, reaction limitation area was not achieved. It can be also concluded that, in the experimental range, bioreaction occurs faster than mass transfer.

Counter-current operation was fundamental to promote absorption. Its effectiveness was assured by the presence of the lower unit the TCE leachate content was treated. As previously observed, lower unit has a great significance at high trickling liquid flow rates and low gas fluxes.

Increasing \( Q_L/Q_V \) ratio produces an increase of the amount of TCE that can pass into the liquid phase and that can be degraded by the lower unit. By varying this ratio, it is
hence possible to split the degradation of the target pollutant carried out by the two trickle bed units; the consequence is the improvement of reactor performance. Experimental results demonstrated an increase of the removal efficiency from 67 to 87% by increasing $Q_L/Q_V$.

However, $Q_L$ cannot be too much high: with an excessive flow rate, water content inside the bed could reduce the cross sectional area for gas flowing, causing clogging, flooding and high pressure drops.

Further studies are required to evaluate the real effects of $Q_L/Q_V$ ratio on the removal efficiency, in order to determine a reliable procedure for assessing the more suitable conditions for mass transfer optimization. A further important challenge in biofiltration studies could be an approach by which the absorption phenomena could be completely understood.

The effectiveness of the BTF design considered can be evaluated by a simple comparison with other studies dealing with TCE removal. Data of removal efficiency, elimination capacity and pollutant concentration in the waste gas are listed in table (9.2). Apart from Yoon, Park whose values differ a lot from the other reports, the present study revealed a good maximum elimination capacity, more than four times higher than the other BTF applications.

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>TCE$_{in}$ [g/m$^3$]</th>
<th>RE [%]</th>
<th>EC [g/(m$^3$.h)]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>0.04-2.42</td>
<td>0.04-16.3</td>
<td>Sun, Wood (1997) [109]</td>
<td></td>
</tr>
<tr>
<td>BF</td>
<td>0.16</td>
<td>30-60</td>
<td>1.9</td>
<td>Cox et al. (1998) [20]</td>
</tr>
<tr>
<td>BF</td>
<td>9.10-9.90</td>
<td>63.7-91.4</td>
<td>166-378</td>
<td>Yoon, Park (2002) [118]</td>
</tr>
<tr>
<td>BF</td>
<td>0.006-1.15</td>
<td>15-95</td>
<td>0.89-1.61</td>
<td>Jung, Park (2005) [60]</td>
</tr>
<tr>
<td>BTF</td>
<td>0.062</td>
<td>82-86</td>
<td>1.17-1.25</td>
<td>Den et al. (2004) [29]</td>
</tr>
<tr>
<td>BF</td>
<td>0.12-0.72</td>
<td>63-75</td>
<td>0.25-0.75</td>
<td>Lackey et al. (2002) [71]</td>
</tr>
<tr>
<td>FEBR</td>
<td>0.06-0.12</td>
<td>82-96</td>
<td>9-28</td>
<td>Kan, Deshusses (2006) [63]</td>
</tr>
<tr>
<td>BTF</td>
<td>0.001-0.19</td>
<td>50-86</td>
<td>0.05-5.62</td>
<td>present study (2008)</td>
</tr>
</tbody>
</table>

Table 9.2: Comparison among some different studies from literature and the present study.

In conclusion, the new BTF design was successful and the introduction of the lower unit could be a good mean to allow counter-current operations.

The gas flow passing throughout the lower packing is a limit for this new design, since a compressor or an air pump is required to provide oxygen for microbial activity. Anyway, this gas flow rate should be moderate in order to reduce the stripping of pollutants and, at the same time, to force biological reaction.

**Conclusions** The capability of a new biotrickling filter design for the treatment of TCE vapours was investigated. The employment of a mixture of inert and organic carrier allowed long-term operation, while the introduction of a lower unit reduced the limits of counter-current mode of operating in biofiltration processes. Tests were carried out in diffusion limitation region, so that mass transfer was the rate determining step of the process. Data obtained for $EC_{max}$ and $RE$ were promising if compared with other studies concerning TCE degradation. In spite of this encouraging results, it was demonstrated that the BTF performances could even be better if operating with adequate gas and trickling water flow rates. The Ottengraf’s modified model was herein tested, and fitting demonstrated a good agreement between calculated and experimental data, with a coefficient of determination $R^2$ of 0.921.
Respirometry is a widely used technique to evaluate the interaction between a substrate and a biomass, by means of the indirect measurement of the oxygen consumption rate.

During the ages, it has become a very significant procedure for the management and the design of wastewater treatment plants (WWTPs), since it involves a simple equipment and it can provide reliable and useful data.

For these reasons, respirometry has been successfully applied also to determine compost stability [52, 72], which is basically a measurement of the content of degradable organics inside the solid matrix.

This technique has not been yet used to evaluate the degradation of volatile organic compounds (VOCs) from a water phase. This situation always occurs in biofiltration process, since pollutants should pass into the water phase in order to be degraded by the biomass. Moreover, the reported studies on compost stability assure the feasibility of the application of respirometry for such organic material, which has been widely used as carrier for biofilter and biotrickling filter equipment.

Since their high volatility, the respirometric analysis of VOCs requires special regards in order to assign the overall removal efficiency exclusively to the biodegradation, limiting any stripping effect.

Some researches [5, 94], however, have employed respirometry in biofiltration process. Such studies were conducted with peat and vermiculite as packing material and dealt only with the simple analysis of biomass activity in long-term operations: VOC-biomass interaction was thus not considered.

In this chapter, the realization of a simple equipment for respirometric analysis is also described. This equipment is basically constituted by some oxygen probes, a multimeter and some simple electric circuits and allows the automatic management of long-term analyses.

10.1 Basic principles

Respirometry is based on the following mass balance:

\[ (-\Delta S) + (-\Delta O_2) = \Delta X \]  

\[ (10.1) \]

where \((-\Delta S)\) is the total substrate consumed, \((-\Delta O_2)\) is the oxygen consumed, and \(\Delta X\)

\[ ^1 \text{This term is more generally referred to the amount of electron acceptor which is reduced during the process.} \]

In the case of respirometry, oxygen is the electron acceptor.
is the biomass generated. 

\( (-\Delta S) \) and \( \Delta X \) are usually related by the yield factor \( Y \), which is defined as the amount of biomass generated for unit of consumed substrate:

\[
Y = \frac{\Delta X}{(-\Delta S)} \quad (10.2)
\]

With this assumption, when one term of equation (10.1) is known, the others are unequivocally determined.

Equation (10.1) can be written in terms of consumption or generation rates as follows:

\[
\frac{dO_2}{dt} = \frac{dS}{dt} - \frac{dX}{dt} \quad (10.3)
\]

Using Monod’s growth model, the two terms on the right can be written as:

\[
\frac{dS}{dt} = \frac{\mu_{max}}{Y} \cdot \frac{S}{K_S + S} \cdot X \quad (10.4)
\]

\[
\frac{dX}{dt} = \mu_{max} \cdot \frac{S}{K_S + S} \cdot X - k_d X \quad (10.5)
\]

where \( \mu_{max} \) is the maximum growth rate \( [\text{time}^{-1}] \), \( K_S \) is the half-velocity constant for the specific substrate \( [\text{g COD/m}^3] \) and \( k_d \) is the endogenous decay coefficient \( [\text{g biomass/(g biomass-time)}] \).

Using these equations, the kinetic parameters can be determined by the measurement of the oxygen consumption rate. These parameters are characteristic of the interaction between the biomass and the substrate.

OUR (Oxygen Uptake Rate) is the most important value, which can be determined by respirometry. Many studies have rather referred to SOUR values (Specific Oxygen Uptake Rate), defined as the OUR per unit of mass of biomass.

Substituting equations (10.4) and (10.5) into equation (10.3), OUR and SOUR can be calculated as follows:

\[
OUR = \left[ \left( 1 - \frac{Y}{Y} \right) \cdot \frac{\mu_{max} S}{K_S + S} + k_d \right] \cdot X \quad (10.6)
\]

\[
SOUR = \left( 1 - \frac{Y}{Y} \right) \cdot \frac{\mu_{max} S}{K_S + S} + k_d \quad (10.7)
\]

Microorganisms require oxygen even if substrate is not available. This consumption is due to the hydrolyzation of dead cells, to their mobility, and to cellular duplication and it is normally called endogenous respiration, to separate it from the exogenous respiration, which is associated to the substrate utilization rate.

During the respirometric test, the measured OUR is determined by the sum of the endogenous and exogenous respirations. To separate the two contributes, a preliminary measurement of endogenous activity is required.

The endogenous contribute can be determined, operating without a substrate, and, from equation (10.6) fixing \( S=0 \), it results:

\[
\frac{OUR}{X} = k_d \quad (10.8)
\]
10.2 Respirometer

OUR values depend on the specific interaction between a biomass and a substrate. This interaction is more intense as the biodegradability of the substrate increases. In complex wastes, soluble organic matter can be fractionated in readily biodegradable (rbCOD), slowly biodegradable (sbCOD) or non-biodegradable (nbCOD) substrate.

During respirometric tests with domestic or industrial wastes, a decrease in OUR values is observed owing to the degradation of different substrates with different biodegradability rates.

By studying these variations of OUR values, a fractioning of the waste based on its biodegradability is possible and it is one of the most important results available with respirometry.

10.2 Respirometer

Respirometers are reactors in which a biomass and a substrate are introduced. Different concepts of respirometer have been used during the years and the main differences consist in the way employed to supply oxygen and water to the system and to measure the dissolved oxygen (DO).

DO can be directly or indirectly measured. Direct systems are mainly electrochemical and employ a DO polarographic sensor (Clark’s cell) immersed into the water phase. Indirect systems measure the reduction of the pressure inside the respirometer, which is due to a chemical absorption of the CO$_2$ (as equimolar product of bio-oxidation) into an alkaline solution.

Respirometers can be open or closed if they have or not any material stream, liquid or gaseous [105].

The most common respirometer employs a DO sensor, with a fixed liquid phase and an intermittent gaseous stream. A scheme of this kind of bioreactor is represented in figure (10.1).

Bioreactor is immersed in a thermostatic bath to assure constant temperature. A magnetic stirrer allows homogeneous conditions inside the reactor. DO and temperature are continuously monitored and data are stored in a computer by means of a data logger unit. Data logger can also activate a pump, as soon as DO inside the reactor is depleted.

A porous diffuser is employed to generate micro-bubbles in order to promote oxygen absorption into the liquid phase.

10.3 Respirometric analysis

In a respirometer, biomass activity reduces the amount of dissolved oxygen. DO concentration vs. time is normally linear and its slope is equal to OUR.

The linear profile can be affected by two main different phenomena: lack of oxygen and changes of substrate fraction that is degraded.

At low DO concentration (about less than 2 mg/l), kinetics of substrate utilization is affected by a new term, whose contribute increases as DO decreases. Indeed, equation (10.4) can be rewritten considering also the contribute of oxygen concentration:

\[ \frac{dS}{dt} = \frac{\mu_{max}}{Y} \cdot \frac{S}{K_S + S} \cdot \frac{S_{O_2}}{K_{O_2} + S_{O_2}} \cdot X \]  

(10.9)
To limit oxygen lack effect on the OUR, fresh air is supplied to the system as DO reaches the value of 2 mg/l, in order to increase oxygen concentration.\footnote{The reported analytical method is the one that has been used in the Chemical Design Laboratory, (DICAMP) Department of Chemical, Environmental and Raw Materials Engineering, University of Trieste.}

The second effect allows the calculation of the biodegradable fractions of the waste: rb-COD, sbCOD and nbCOD.

In long-term tests, DO profile vs. time has an asymmetrical sawtooth shape, with zones with negative slopes generated by biomass activity, and zones with positive slope, corresponding to the air supply. An example of a respirogram is represented in figure \ref{fig:respirogram}.

To evaluate the kinetic parameters from the study of OUR values, also other parameters are necessary. The amount of substrate and biomass at the beginning and at the end of the experiment have to be calculated. Substrate is usually calculated as COD value and biomass as VSSs (volatile suspended solids).

### 10.4 Respirometry for compost stability

Stability is a very important parameter for characterizing the quality of a compost and it is related to the amount of biodegradable substances inside it. Standard methods to assess compost stability is based on the determination of the respirometric index \cite{131}, which relates the consumption of oxygen to the amount of organic matter.
10.4. Respirometry for compost stability

![Graph 1](image1)

**Figure 10.2:** Typical profile of DO vs. time curve. Positive slopes correspond to aeration; negative slope to biomass respiration. Endogenous regime occurs in the first test period. Data obtained with an industrial waste at DICAMP, University of Trieste.

![Graph 2](image2)

**Figure 10.3:** OUR profile in time. Data obtained with an industrial waste at DICAMP, University of Trieste.

This kind of test is carried out working without a water phase. In these conditions, there is a bad contact between biomass and biodegradable substances and the moisture level can be a problem. For these reasons, some investigations have tried to extend respirometric techniques to the determination of compost stability [72].

**Compost stability and UNI standards** UNI has fixed some rules to determine the respirometric index [151]. Tests should be carried out in a sealed system of 22 liters, using 1 kg of compost with a humidity of 80%. In the same vessel, a beaker with a solution of NaOH 2N is used to chemically absorb the CO₂ generated from the biological activity. This absorption reduces the pressure inside the system which is continuously monitored.

The respirometric index ($IR$) $[\text{mgO}_2/(\text{kgVSS-h})]$ can be calculated with this equation:

$$IR = V_g \cdot \frac{\Delta P_{\text{max}}}{1013} \cdot \frac{32}{24.04} \cdot \frac{1000}{V_{SS_{\text{dry}}}} \cdot \frac{1000}{t}$$  

(10.10)

where $V_g$ is the volume of the system occupied by the gas [l], $\Delta P_{\text{max}}$ is the negative pressure obtained at the maximum slope of the curve $\Delta P$ [mbar], $V_{SS_{\text{dry}}}$ is the amount of volatile solids in the compost sample [Kg/Kg] and $t$ is the time from the beginning of the test to the time at which $\Delta P = \Delta P_{\text{max}}$. 
Respirometric approach Lasaridi and Stentiford [72] have described a simple procedure to use respirometry to assess compost stability. Tests were carried out in the water phase, monitoring the DO concentration. Respirometer type is LFS [105], with static liquid and discontinuous aeration.

This kind of approach has the advantage to reduce the resistance to the mass transfer between gas and liquid phases and to be not affected by variations in the moisture level of the compost. Moreover, it has demonstrated to achieve more suitable results, compared with other stability tests.

10.5 Design and set-up of a simple equipment for respirometry

Respirometry test requires long times for the complete oxidation of the substrates and the achievement of new endogenous conditions. This time depends on biomass and substrate concentration: however, tests shall be carried out for longer than one day.

An automatic system is therefore necessary to store DO data and to activate the aeration system in oxygen lack conditions.

In this section, a simple respirometric equipment designed and set-up in order to carry out long-term respirometric analyses is described.

This equipment was set for three independent respirometric lines. In this way, a simultaneous analysis with three different conditions could be achieved.

10.5.1 Materials

Respirometer was an acrylic glass vessel 1 liter volume ($\Phi_{in}$ =11 cm). Its content was stirred by a magnetic stirrer and its temperature was kept constant by a thermostatic jacket controlled by a cryothermostat ISCO GTR2000 with external recirculation pump.

Dissolved Oxygen was measured by a Clark-type polarographic probe Hanna HI 76407/4, connectible to the portable oxymeter Hanna HI 9143. Aeration system included a membrane volumetric pump from SHEGO, with nominal fed of 150 l/h and a porous diffuser immersed in the liquid.

Temperature was measured by a Pt100-type RTD (Resistance Temperature Detector) with 4 wires. Temperature was continuously monitored inside the respirometer and for the oxygen probe calibration.

The data-logger/switch unit Agilent 34970A was employed for data-logging and process controlling. It was equipped with HP 34901A multiplexer plug in with 20 input channels and the multifunction module HP 34907A. This device was used to store data into a computer and to activate the pumps, as DO value reaches its lower set limit.

10.5.2 DO probes connection

Clark’s cell polarograph is based on an electrochemical reaction which involves oxygen in a solution of KCl under a voltage of 400-1200 mV. This reaction generates an electrical current proportional to the concentration of oxygen.

Oxygen probes Hanna HI 76407/4 have three cables connected to anode, cathode and the last one which closes the circuit of the thermistor. Temperature is necessary to the calibration when passing from saturation values to mg/l.
A device was realized to provide a sufficient voltage to the probe and to elaborate the electric signal.

A power supply unit was employed to generate a stable continuous current at 1.5 V. This voltage was converted in a 750 mV voltage by a simple voltage divider, with two resistors of 2.7 kΩ.

At this voltage, the current signal was about 1-2 µA. This value was too low, since the noises on the line had the same amplitude. With a resistor, it was possible to pass from a current measurement to a voltage measurement. Resistor was of 10 kΩ.

The voltage across the resistor was connected to the multichannel plug-in of Agilent 34970A and continuously monitored.

Figure [10.4] shows a diagram of the DO probes connection.

![Circuit diagram of the equipment for DO probes connection, with the autosupply system.](image)

**Figure 10.4:** Circuit diagram of the equipment for DO probes connection, with the autosupply system.

**DO probe calibration**

A calibration is required, to pass from a voltage signal to values expressed in mg/l. Current and voltage as well are proportional to dissolved oxygen concentration and signal is about 0 when DO concentration approximates 0.

However, two points are required for the calibration. Zero-Oxygen condition can be obtained with a zero-oxygen solution. The second point for calibration can be obtained under saturation conditions, placing the probe in air. The voltage value obtained in such conditions is equal to 100% of saturation.

To pass from saturation percentage to mg/l, temperature is required since this value is temperature dependent. However, many data are available to correlate temperature, oxygen saturation and oxygen concentration.

Temperature was measured by Pt100 thermistor, connected to the data-logger as well.
Temperature calibration is not required since the proportionality constant remains fixed.

10.5.3 Aeration control

Aeration system provides oxygen for substrate removal. Oxygen should be supplied to the reactor as soon as DO value reaches some specific threshold, below which first-order kinetic effects the oxygen consumption.

Agilent 34970A has the possibility to associate any channel to an alarm output. 4 alarm outputs are possible: each one generates a TTL (Transistor-transistor logic) impulse signal as the measured value pass some high or low limit. TTL voltage values can vary from 0 to 5 V.

TTL signal has not enough power to activate any device. It can be connected to the base of a BJT transistor that can work as a switch. Emitter and collector are connected to a relay and to 5V external voltage. When TTL signal is zero, no current passes from the collector to the emitter and the relay circuit is open. When the signal is other than zero, the relay circuit is closed and the relay is switched to activate any further device.

A circuit diagram is represented in figure (10.5). Resistance is required for the correct transistor polarization, while the diode served to screen transistor from relay current. A voltage of 5 V in c.c. has been used to switch the relay. Figure (10.6) shows the final adapter used to pilot the relay with a TTL signal.

\[ R = R_0(1 + \alpha T) \]

For a Pt100 sensor, \( \alpha = 0.00285 \) and \( R_0 = 100\Omega \)

Timers Omron H3CR-A8EL have been used to control the aeration. Their poles were set in order to obtain an output signal which can be positive for the period set by the timers themselves. With this arrangement, timers will work independent on the duration of the input signal and they are activated only by changes in the input signal.

Indeed, some seconds after the beginning of the aeration, DO value becomes higher then the lower fixed limit and TTL signal expires. An autosupply mode allows prolonged aeration.

---

\[ \text{Figure 10.5: Circuit diagram of a BJT transistor as switch used to pilot a relay with a TTL signal.} \]
10.5. Design and set-up of a simple equipment for respirometry

Timers are connected to some volumetric pumps and to the power supply unit as shown in figure (10.8).

**Figure 10.6:** Circuit diagram of the adapter used to pilot relay with a TTL signal.

**Figure 10.7:** Circuit diagram of timer (T) with the autosupply system.
Conclusions  Respirometry is an useful and simple technique employed to study the interaction between a biomass and a substrate. It can be used for the calculation of kinetic constants for WWTP, to assess compost stability, and to determine the activity of biofiltration microorganisms. Promising results can be obtained by using VOCs as the substrate. A simple respirometric equipment was realized to carry out long term automatic tests. The knowledge of some simple electronic basics is necessary to understand the functioning of DO probes and thermistors and to use electrical and logical signal to pilot some simple device. The new equipment has made the test easier and several analyses have been already carried out since this equipment was realized. Many tests have been carried out with municipal and industrial wastewaters, but also with a solid matrix as compost. Data resulted reliable and kinetic parameters obtained by OUR analysis were successfully compared with data form literature with.
Respirometric techniques are here employed to evaluate the kinetics of TCE degradation and to assess biomass activity on a compost sample. The aim of this study is to verify if such technique can be successfully applied in the biofiltration field. Indeed, some useful hints can be obtained from respirometry, like the determination of the most suitable kind of biomass, the estimation of toxic or inhibitory limits for a specific pollutant, or even to verify the effects of pH and temperature on the kinetics of biological phenomena.

Tests were carried out in a respirometer (LFS type 105), with discontinuous aeration and automatic control system. The equipment employed in these tests was the one described in chapter 10.

Initially, the indexes of compost stability have been determined and results were compared with data from the literature [72]. Afterwards, biomass was conditioned with a specific nutrients solution and than with an increasing amount of trichloroethylene.

11.1 Materials and Methods

11.1.1 Respirometer and respirometric equipment

Respirometry was carried out in three acrylic glass reactors 1 liter volume each. Reactors were immersed in a thermostatic bath for temperature control. Each reactor was provided with a dissolved oxygen probe and a temperature sensor and it was stirred with a magnetic stirrer.

DO and temperature data were continuously monitored and stored in a computer. An automatic system was employed to switch on some air pumps to introduce additional oxygen to the system for the complete oxidation of the substrate.

A more detailed description of the respirometers is reported in chapter 10.

11.1.2 Fundamental procedure

At start-up, each reactor was filled with the different system biomass/water under investigation, without additional nutrients or pollutants. The content was kept under continuous aeration to saturate the reactor with oxygen.

Subsequently, aeration was switched off and biomass started consuming the DO. The time courses of dissolved oxygen are usually linear and the slope is the Oxygen Uptake Rate (OUR). At the beginning, the only contribution to OUR derives from the endogenous respiration.
After having determined the endogenous OUR, nutrients were supplied to the system. Oxygen consumption rate occurred faster since the additional contribution of substrate oxidation.

Further aeration was supplied once DO values reached the lower imposed limit of 2 mg/l. Below this limit, it was supposed that linearity between time and DO expired because oxygen lack. Aeration lasted 1 minute and was automatically switched off during the whole experiment.

11.1.3 Analysis

Dissolved oxygen concentration was measured by some polarographic probes and the temperature was controlled by a Pt100 sensor with 4 wires. VSS and TS were determined according to the standard methods and COD by a colorimetric method. TCE concentration in the liquid was measured by a GC/ECD static head space method as described in chapter (7).

11.1.4 Compost properties

The compost sample under investigation came from a composting plant treating municipal solid wastes. It had 31% humidity and 0.638 gVSS per gTS (dry basis). Its density was about 0.510 Kg/m³.

11.2 Compost stability

Compost is characterized by a big amount of biodegradable substances, whose fermentation may generate odours, reduce the pH, and change the physical and biological properties of the compost itself.

Stability is a term used to define the amount of this kind of substances not yet fermented and it plays an important role for the compost re-utilization in agriculture.

The evaluation of compost stability can be very important to assess the amount of native nutrients and microorganisms while using compost in biofilters or biotrickling filters.

11.2.1 Operating procedure

About 1 kg of compost sample was heap sampled to have some homogeneous amounts. Ten grams of compost (wet basis) were put into each respirometer with 750 ml of water, so that 9.2 gTS/l and 5.86 gVSS/l were supplied to the system. Temperature was set about 20°C. Some grams of ATU (allyl-thio-urea) were added to inhibit nitrification.

DO concentration was continuously monitored along 140 hours with a scanning interval of 15 seconds. Lower DO limit was set at 2 mg/l and the duration of aeration at 1 minute. OUR values were calculated with the software OUR generator, which is under development at DICAMP, Department of Chemical, Environmental and Raw Material Engineering, University of Trieste.

TS, VSS and COD on the filtrate were measured at the end of the test, by using the standard methods.
11.2. Compost stability

11.2.2 Results and discussion

Figure 11.1 represents the OUR profile which was obtained by compost respirometry in each of the three reactors in parallel.

![Figure 11.1: OUR analysis for assessing compost stability. The same compost amount generated different OUR profiles in reactors 1, 2 and 3.](image)

It should be noticed that biomass activity remained negligible for about 12 hours. After this time, it suddenly increased to reach its maximum value after 30-35 hours from the beginning of the test. Afterwards, it showed a very abrupt decrease and a prolonged oscillation of OUR values (0±4 mgO₂/(l·h)) from hour 60 till the end of the experiment.

This behaviour can be explained by considering that, at the beginning of the test, both biomass and nutrients are attached, and that a few hours are required for their solubilization. After this process, microorganisms can easier have at disposal oxygen and nutrients, so that the kinetic rate increased.

The same effect can be considered to be responsible of the OUR fluctuation at the end of the test: some nutrients could be solubilized only after several hours. This hypothesis can be confirmed by the fact that the same behaviour in OUR curves for reactors 1 and 2 at about 115 hours was obtained.

With respect to the fast reduction in OUR values, this effect can be caused by the complete oxidation of some readily biodegradable COD (rbCOD).

At the end of the test, the (compost/water) suspension had a complete different appearance. Solid particulate was limited to some little stone or glass and plastic fragments and all the organic fraction had passed into solution. Biomass was concentrated at it showed good settleability properties (7.9 gTS/l and 6.18 gVSS/l).

The average residual COD on the filtrate was equal to 546 mg/l. It can be supposed that this was the amount of the inert or non-biodegradable COD (nbCOD) present in the compost.

As proposed by LASARIDI and STENTIFORD, the specific maximum rate SOUR ex-
### Table 11.1: Average values of TSS, VSS and COD measured before and after the test to assess compost stability.

<table>
<thead>
<tr>
<th></th>
<th>Initial Values</th>
<th>Final Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>9.2 [gTS/l]</td>
<td>7.9 [gTS/l]</td>
</tr>
<tr>
<td>VSS</td>
<td>5.86 [gVSS/l]</td>
<td>6.18 [gVSS/l]</td>
</tr>
<tr>
<td>COD</td>
<td>-</td>
<td>546 [mg/l]</td>
</tr>
</tbody>
</table>

Table 11.1: Average values of TSS, VSS and COD measured before and after the test to assess compost stability.

Pressed in [mgO$_2$/gVSS·h] can be calculated with the following equation:

\[
SOUR = \frac{\|S\|_{max} \cdot V_{resp}}{M \cdot DS \cdot VS} \tag{11.1}
\]

where $\|S\|_{max}$ is the absolute maximum OUR value [mgO$_2$/l·h], $V_{resp}$ is the volume of the suspension [l], $M$ is the mass of the compost [g on wet basis], $DS$ is the fraction of dry solids [gTS/g] and $VS$ is the fraction of volatile solids [gVS/gTS].

The cumulative oxygen demand was also calculated in the first 60 hours of operation (OD$_{60}$). This assumption strongly differs from other investigations, which have taken into account this value referred to the 20th hour. In the present work, OUR values were not significant before such time, and a longer period should be considered.

OD$_{60}$ has been calculated as follows:

\[
OD_{60} = \frac{V_{resp}}{m \cdot DS \cdot VS} \cdot \int_{t=0}^{60} \|S\| \cdot dt \tag{11.2}
\]

Integrating the OUR curves, it is possible to determine the amount of biodegradable substrate, expressed in mgCOD/l, which has been utilized by the biomass during the experiment:

\[
COD_{140} = \int_{t=0}^{t=140} OUR \cdot dt \tag{11.3}
\]

Since OUR values at hour 140 approximate zero, it can be established that COD$_{140}$ is equal to the overall amount of biodegradable matter inside compost sample.

Data are reported in table (11.2).

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$|S|_{max}$ [mgO$_2$/l·h]</th>
<th>SOUR [mgO$_2$/gVSS·h]</th>
<th>OD$_{60}$ [mgO$_2$/gVSS]</th>
<th>COD$_{140}$ [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.354</td>
<td>2.786</td>
<td>50.177</td>
<td>372</td>
</tr>
<tr>
<td>2</td>
<td>7.448</td>
<td>1.269</td>
<td>38.089</td>
<td>394</td>
</tr>
<tr>
<td>3</td>
<td>11.209</td>
<td>1.910</td>
<td>44.804</td>
<td>317</td>
</tr>
</tbody>
</table>

Table 11.2: Results from compost stability analysis.

Our present SOUR and OD$_{60}$ values strongly differ from other authors [72]. This fact can be due to a different compost stability or to a different compost origin. Indeed, since it comes from a municipal solid waste composting plant, compost can have very different composition and properties.
11.2. Compost stability

It should be noticed that the three respirometers have shown different behaviour (SOUR value in reactor 1 more than twice the one in reactor 2), even if they worked at the same conditions. Compost samples could likely not be representative, having different composition, different biomass concentration or even different moisture.

Probably, the low compost concentration (10 grams of compost in 750 ml of water) can be responsible of such behaviour, like other case referred in literature [72].

COD data are instead comparable, since maximum and minimum values differ only of 20%. This may suggest that COD could be more representative of the amount of biodegradable matter inside the compost.

Indeed, $∥S∥_{\text{max}}$, SOUR and OD are basically related to the degradation rate. Therefore, they depend on the characteristics of the organic substances and on their fractioning in readily and slowly biodegradable COD. Moreover, since solubility plays an important role in this kind of analysis, the physical dimension of the organic matter can be determining for the biodegradation rate.

A COD balance can be outlined to evaluate $\xi$, the amount of COD per gram of TS solubilized:

\[
\text{Accumulation} + \text{VSS} + \text{COD degraded} + \text{TS solubilized} = (0.546 - 0) + (6.18 - 5.86) \cdot 1.45 + (0.372 + 0.394 + 0.317)/3 = -(7.9 - 9.2) \cdot \xi
\]

where 1.45 is the mass of COD per unit mass of VSS [81]. All data are reported in g/l. Since initial and final COD, TSS and VSS were average values, also the degraded COD is calculated with the arithmetical mean of the values from the three respirometers.

By calculation, $\xi$ results equal to 1.05 gCOD/gTS solubilized. Compost under investigation has therefore the following composition: 85.9% grams of non-soluble TS, 8.2% of biodegradable COD, and 5.9% of non-biodegradable COD per gram of total solid. Biodegradable COD was partially converted into VSS (61.5%) and partially used by microorganism activity (38.5%).

It should be noticed that VSS value at the beginning of the test is related both to biomass concentration and to soluble COD. Indeed, during incineration, biomass and soluble COD both evaporate and they are thus included in the volatile organic stuff. Thereof, since no additional COD was supplied to the system, the increase in VSS concentration was likely due to oxygen supply and can be explained only supposing a different level of oxidation of the VSS.

At the end of the experiment, a pH value of 7.41 was measured. In spite of the degradation of organic substances that usually leads to acidification [67], buffer capacity of compost could keep pH close to 7.

11.2.3 Possible applications to biofiltration

Some useful hints can be obtained by this respirometric analysis.

The amount of soluble fraction of compost can be calculated. This means that compost inside a biofiltration equipment is partially soluble (around 14%) and its weight is thus reduced.

Soluble and biodegradable COD can be readily consumed and a big amount of inert COD (about 6%) can be stored inside the bed and in the leachate of a biotrickling filter.
As it was previously described (see section 9.1.4), the COD measurement in the leachate can be strongly affected by the presence of this big amount of no biodegradable COD, so far that the determination of the biomass activity by nutrients consumption is not possible. That was because the contribute of the nutrients solution to the overall content of organic substances was negligible compared to the nbCOD introduced with compost.

11.3 TCE effects on compost activity

After the characterization of the original properties of the compost, a new study was carried out to evaluate the effects of trichloroethylene on its activity.

The new experiments involved the suspension obtained from the stability assay. The content of the three respirometers was mixed together to restore homogeneous conditions. During mixing, a great amount of biological foam was generated. This might be due to a competition among different microbial species grown in each of the three respirometers during the previous test.

Foam is a problem for respirometric analysis, since it can flush out some volumes of the suspension during the aeration steps. To remove the foam, mixture was kept under prolonged aeration and some readily biodegradable COD was added.

In some days, foam was strongly reduced and test could be attempted.

11.3.1 Operating procedure

Two different tests were carried out in sequence with the same system.

Test #1 intended to condition the biomass with a diluted solution containing some readily biodegradable nutrients, in order to calculate the \( \text{SOUR}_{\text{max}} \) without pollutant.

Test #2 involved also an aqueous solution of TCE at different concentrations, and the maximum SOUR values were compared with data from the previous test.

**Test #1**

Three respirometers were filled each with 740 ml of the mixture of biomass obtained from compost. DO concentration and temperature were measured every 15 seconds. Oxygen lower limit was set at 2 mgO\(_2\)/l.

The suspension introduced in the reactor had 4.80 gTS/l and 3.15 gVSS/l.

In this experiment, a synthetic solution of nutrients was prepared in order to introduce 50 mgCOD/l by adding 10ml of solution. Nutrients solution was constituted by Sodium Acetate, Glucose and Ethanol: their concentration was set in order to give the same contribution to the COD by each of the three different substrates (table (11.3)). All these nutrients were considered to be readily biodegradable.

**Test #2**

Test #2 was carried out 6 days along, with a daily addition of 10 ml of concentrated solution of nutrients (table (11.3)), in order to reach 300 mgCOD/l inside each reactor, and 40 ml of TCE solution at different concentrations.

Experiment was performed with a mixture among of the contents of the respirometers employed in test #1. Mixing was necessary to restore homogeneous conditions.

Each respirometer was initially filled with 750 ml of solution with 4.78 gTS/l, 3.17 gVSS/l and 299 mg/l of inert COD. Every day, 50 ml of supernatant were sampled from each reactor.
11.3. TCE effects on compost activity

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Concentration [mg/l]</th>
<th>COD equivalent [gCOD/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diluted</td>
<td>Concentrated</td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>1620</td>
<td>9720</td>
</tr>
<tr>
<td>Glucose</td>
<td>1302</td>
<td>7812</td>
</tr>
<tr>
<td>Ethanol</td>
<td>600</td>
<td>3600</td>
</tr>
</tbody>
</table>

Table 11.3: Composition of the nutrient solution employed in respirometric analysis.

and analyzed to determine the amount of VSS, TSS, COD and residual TCE. Ten minutes before the sampling, stirrers were switched off to allow sludge settling, reducing the amount of biomass removed from the reactors by sampling the supernatant. Endogenous decay was thus determined by the measurement of DO inside the respirometers.

After some minutes, 40 ml of TCE solution was added in different concentrations to the three systems. First reactor was filled only with water and served as blank. In the other two vessels, after the addition of the pollutant, there were 18.7 and 36.4 mg/l of TCE respectively.

TCE effects on biomass activity could be evaluated, comparing the values of OUR obtained before and after TCE additions.

Some minutes later, 10 ml of concentrated nutrients solution was introduced in each reactor and respirometric analysis was exploited as described before.

11.3.2 Results and discussion

Test #1

Figure (11.2) reports OUR data obtained during test #1.

OUR profiles are quite similar in the three reactors, with comparable values of ||S||ₘₐₓ. However, as reported in table (11.4), the consumed COD, which was calculated from the integration of the OUR curves, differs a lot.

This is likely due to any changes in the characteristics of the biomass and/or to an oxygen probe malfunctioning. Indeed, gap of OUR data was more marked after 10 hours from the beginning of the test, and at that time the two mentioned problems can show a greater effect.

VSS during the test did not vary too much (less than 5%) and COD did not accumulate inside the reactors.

For further experiments, it should be useful to define the maximum specific OUR, SOURₘₐₓ [mgO₂/(gTS·h)], with an average value of ||S||ₘₐₓ data reported in table (11.4) and a volatile concentration of 3.15 gVSS/l. For the specific suspension and substrate, SOURₘₐₓ was equal to 4.843 mgO₂/(gTS·h).

Test #2

TCE effects on biomass activity can be observed in graph (11.3), in which the black arrows approximately indicate the moments at which nutrients and TCE had been supplied to the system.
Higher quantities of TCE caused stronger decreases in the biological activity. This can be seen comparing profiles 1 and 2, which were obtained introducing 18.7 and 37.4 mg/l of TCE respectively.

Another remarkable result is the partial reduction of OUR during the test for both profiles, so that the final OUR value is much lower than the one measured in endogenous conditions at the beginning of the test. This may be due to a reduction in the viable biomass, to a partial deactivation of microbial activity, or to an accumulation of toxics.

The drop in $||S||_{max}$ is even more significant. While in the first addition, nutrients supply suddenly generated an increase in the biomass activity, after the forth addition of TCE its contribution seems to be negligible. This effects is not attributable to TCE accumulation inside the reactors: indeed, TCE measured in the supernatant at the end of the tests was negligible (160 µg/l and 95 µg/l for profile 2 and 1 respectively).

The reduction of OUR and $||S||_{max}$ can be explained supposing that TCE degradation had generated some toxics which limited biomass activity. Changes in the biological community of the two reactors had likely not occurred, since OUR values at the end of the test are comparable for profile 1 and 2, even if they had operated at different conditions.

Figures 11.4 and 11.5 report the time course of dissolved oxygen for profile 1 and 2, during the first TCE and nutrients addition during the first day. It can be observed that TCE reduced the oxygen consumption rate in both cases. On the contrary, the subsequent addition
11.3. TCE effects on compost activity

Figure 11.3: OUR data obtained with additions of TCE and nutrients in sequence. Nutrients were supplied to have 300mg/l of fresh readily biodegradable COD inside each reactor.

of nutrients generated an increase in the biological activity.

OUR values do not consider the effect of VSS dilution due to TCE and nutrients addition. SOUR is thus more representative of the process and the calculated data are reported in table (11.5) for all the subsequent addition, in comparison with SOUR\textsubscript{max}.

<table>
<thead>
<tr>
<th>day</th>
<th>Profile 1 SOUR (mg/(gVSS·h))</th>
<th>Profile 1 SOUR/SOUR\textsubscript{max} (%)</th>
<th>Profile 2 SOUR (mg/(gVSS·h))</th>
<th>Profile 2 SOUR/SOUR\textsubscript{max} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Endogenous decay</td>
<td></td>
<td>Endogenous decay</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>with TCE 1.233</td>
<td>25.5</td>
<td>with TCE 1.266</td>
<td>26.1</td>
</tr>
<tr>
<td></td>
<td>with nutrients 4.125</td>
<td>85.2</td>
<td>with nutrients 3.442</td>
<td>71.1</td>
</tr>
<tr>
<td>2</td>
<td>with TCE 2.124</td>
<td>43.9</td>
<td>with TCE 1.183</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>with nutrients 4.008</td>
<td>82.8</td>
<td>with nutrients 2.536</td>
<td>72.4</td>
</tr>
<tr>
<td>3</td>
<td>with TCE 2.440</td>
<td>50.4</td>
<td>with TCE 1.284</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>with nutrients 3.100</td>
<td>64.0</td>
<td>with nutrients 2.647</td>
<td>54.7</td>
</tr>
<tr>
<td>4</td>
<td>with TCE 2.355</td>
<td>48.6</td>
<td>with TCE 1.923</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>with nutrients 2.043</td>
<td>42.2</td>
<td>with nutrients 1.356</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>with nutrients 2.133</td>
<td>44.0</td>
<td>with nutrients 1.939</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Table 11.5: SOUR data for profile 1 and 2 along the subsequent daily addition of TCE and nutrients. SOUR data are calculated fixing 2.1 gVSS/l and they are compared with SOUR\textsubscript{max} calculated in test #1.

TCE reduced oxygen uptake rate to less than the endogenous activity. This fact can be due to both toxic effects and cometabolism.
Biomass had not been acclimated with TCE and the sudden addition of such contaminant could be a shock for the microorganisms. This can be also demonstrated by the fact that this drop below endogenous conditions became less marked considering the overall test.

TCE needs a primary substrate to be oxidised by a biomass. Thus, no increase in OUR values can be achieved introducing TCE only. For this reasons, the determination of the kinetic constants for TCE degradation results particularly stiff.

From the data reported in table (11.3), it can be observed that, considering the whole experiment, SOUR values measured after TCE addition increased. This may be due to biomass
acclimatation, which could better face TCE supply. On the contrary, SOUR measured after nutrients addition strongly decreased, passing from 4.125 to 2.133 mgO₂/(gVSS-h) for profile number 1.

These two contrasting results can be explained supposing a selection in the biomass community, which led to a better TCE resistance, to the biological activity depletion.

The evaluation of the kinetics by means of respirometric techniques is influenced by the high volatility of the pollutant. Really, during aeration steps, some TCE amount can be removed from the reactors by stripping, so that it is not possible to evaluate the contribute of the biodegradation to TCE removal.

Some attempts could be carried out using a very diluted biomass and substrate mixture. In this condition, the oxygen consumption rate should be slow and less oxygen supply is required to allow the complete oxidation of the organic matter.

11.3.3 Possible applications to biofiltration

From the respirometric analysis, TCE was stated to have some toxic effects on native compost biomass. Biological activity decreased with the subsequent addition of pollutant. However, a partial selection of the biomass was revealed.

These main results obtained from the respirometric approach can be useful to evaluate the possibility to apply biofiltration to the treatment of TCE vapours.

Toxic effects and biomass selection influence the start-up period, while the reduction of the biological activity should be taken into account when a TCE-rich gas flows throughout a compost-based bed. Indeed, biological degradation rate of toluene or phenol can vary a lot with or without TCE, as occurred in test #2 with the nutrients solution.

This approach, however, has some limits. First of all, the determination of the kinetic constants is particularly stiff, since the contribution of stripping to the overall removal. Moreover, pollutant was already present in the liquid phase and the mass transfer phenomenon was completely neglected.

Despite that, further experiment should lead to an optimization of this technique. Since its simplicity, respirometry can be widely applied in many laboratories and it can be useful to identify the more suitable biomass for the specific target pollutant, to evaluate the problems concerning the degradation, and to assess toxic or inhibitory limits.
Conclusions

Respirometry was initially applied to evaluate compost stability. The experiment was strongly affected by the heterogeneity of the compost. Indeed, data obtained from three respirometers operating with the same concentration and conditions differ a lot. This result was more marked if kinetic parameters are considered ($|S|_{\text{max}}$, SOUR and $OD_{600}$) rather than the total biodegradable COD. Another problem related to this kind of experiment was the great generation of biological foam. TCE was stated to affect biological activity. A reduction of SOUR values was noticed and this lack became more significant with subsequent pollutant additions. This reduction was also related to the amount of TCE introduced to the system. Moreover, a partially selection of the biomass had likely occurred, since microorganisms better faced TCE addition during the test. The presence of toxics generated by TCE degradation, the performance of DO probes, and the effects of stripping strongly influenced this respirometric approach to biofiltration. However, some useful hints have been obtained by this technique, including the determination of compost organic matter, the evaluation of cometabolism, the study of biomass acclimatization and of toxic effects of the target pollutant.
Conclusions

This research activity concerns the development and the validation of a methodology for the treatment of gaseous pollutants.

Biotechniques were identified as a safe, effective and economic system to control air emissions and to reduce air pollution. The mechanism and the applications of biological removal were investigated and different design solutions were compared to evaluate advantages and drawbacks.

The problems concerning a specific target pollutants were considered to determine the best strategy to control its emission.

A pilot-scale bioreactor was designed and set-up, and its effectiveness was evaluated during long-term operation.

The case study concerned the removal of trichloroethylene (TCE). Biotrickling filter was supposed to be the most suitable bioreactor, since it allows the removal of toxics from inside the bed and it can provide a good surface area for mass transfer.

Two new features marked the pilot-plant under investigation. The first winning feature consisted in the employment of a mixture compost/inert carrier as packed bed: this solution provided high mechanical properties and good buffer capacity to the system, reducing the risk of bed compaction and acidification. The second winning feature was the utilization of a new trickle-bed unit, located below the biotrickling filter, to remove the pollutant from the trickling liquid, enhancing the effectiveness of the counter-current operating mode.

The new biotrickling filter design was successful. It had operated for longer than six months, without revealing malfunctions: pressure drop and pH of the leachate remained quite constant during the whole operation. The maximum elimination capacity and the removal efficiency were equal or higher than those reported in the literature concerning TCE removal, confirming the goodness of the new design.

Along the whole experimental range of concentration, mass transfer phenomena were seen to be the rate determining step of the process. Further investigations on trichloroethylenne removal should thus have a particular attention to absorption effects on the removal efficiency.

In spite this good results, bioreactor performance could be highly enhanced by using a correct ratio between gas and liquid flow rates. The new design permits the pollutant removal to be split into the two bioreactor units, increasing the overall removal efficiency.

A new mathematical model has been proposed and validated with the experimental data. The new model has many advantages, including the possibility to have a simple analytical solution. Fitting showed a good agreement between calculated and experimental data, so that the model could be a good tool for a preliminary bioreactor design.
Some attempts were also carried out in order to apply respirometry for the characterization of the interaction between trichloroethylene and a compost-native biomass. Some good hints arose from this study, including the confirmation of cometabolism and of a partial biomass adaptation to the pollutant. However, the determination of kinetic constants was not possible because of stripping effects.

In conclusion, biofiltration is a promising technique to control air emission, but it is still under development: many aspects are unknown and further studies are required to enhance the performance of the process.

As it was herein demonstrated, the knowledge of the problems related to this technique and to the degradation of the target pollutant are a fundamental requirement for a good process design optimization.

Pollution control should be studied with the deep awareness that the sole compliance with the limits fixed by law should be not enough.
This research was made possible thanks to support from the Italian Ministry of Public Education (MIUR), which offers the fellowship in compliance with the law 170/2003, for the scientific area of “Innovative chemical processes”.

Un ringraziamento particolare al mio supervisore, professor Iginio Colussi, e ai professori Vittorino Gallo e Angelo Cortesi, che mi hanno seguito con estrema disponibilità e attenzione durante queste tre anni. Li ringrazio, inoltre, per avermi permesso di lavorare in un ambiente sereno e pieno di stimoli, godendo della loro fiducia.

Vorrei inoltre ringraziare tutti coloro che hanno lavorato a stretto più stretto contatto con me in dipartimento, in particolare Vincenzo, Rosi, Nicola, Kathia e Lorenzo, e tutti gli amici del DICAMP, passati e presenti.

Grazie anche ai miei coinquilini e al Coro dell’Università che mi hanno permesso di staccare la spina quando ce n’era bisogno.

Y muchas gracias a los compañeros del piso Maestro Clave 1/5, que me hicieron pasar genial mi periodo en España. Y también al profesor Christian Kennes, Yuomin y todos los chicos del laboratorio de Ingeniería Química de la Universidad de A Coruña.

E grasie soredut a ducj chei a cui j puis scrivi par furlan, ai miei gjenitòrs ch’a jan savût seguí il gno lavor cun la juste distacade atenzion, a dute la me fume e a ducj j amis ch’j cjati cuand ch’j torni a Glemone, par une sunade, un caffè, o une partide a cjartis.

J sieri cheste tesi cul stes pinsir cun cui la j’ai tacade, disint grassie a Giuly, che cjape dentri dut ce ch’j fas e cun cui dut al devente facil.


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