Ministero dell'Istruzione,
dell'Università e della Ricerca

UNIVERSITÀ DEGLI STUDI DI SALERNO

Dipartimento di Ingegneria Civile

Tesi di Dottorato
in
Rischio e sostenibilità
nei sistemi dell'ingegneria civile, edile ed ambientale

XXXI (2015-2018)

ADVANCED SOLUTIONS FOR THE ABATEMENT OF VOCs AND ODOURS

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Abstract

In the last decades, atmospheric pollution has become an increasingly alarming problem, due to its adverse effects at the global, regional and local scales.

In this context, the emissions of Greenhouse Gases (GHGs), Volatile Organic Compounds (VOCs) and odours from chemical manufacturing plants, petrochemical sector and other hazardous sources pose a major challenge.

Global warming, due to increased GHGs level in the atmosphere, has been identified as one of the key challenges in this century. Indeed, the impacts of global warming have caused severe damages towards human and environment ecosystem.

VOCs are included among the priority gaseous organic contaminants, with BTEX identified among the most dangerous for human health. They are also considered responsible for the photochemical pollution as a result of their reaction in the atmosphere with nitrogen oxides in presence of solar radiation. In addition, their tendency to volatilize readily to the atmosphere leads to problems connected to odour annoyance.

These aspects triggered the enforcement of stricter regulations and, consequently, boosted the necessity of properly manage atmospheric emissions.

The conventional chemical-physical processes mainly used for the treatment of these kinds of emissions envisage the contaminants transfer to other phases and, thus, the necessity of further treatments. Biological processes and Advanced Oxidation Processes (AOPs), instead, are able to support the degradation and mineralization of organic compounds, resulting in more effective solutions. Furthermore, AOPs applied as pretreatments at biological processes may improve VOCs biotreatability and control the accumulation of biomass.

Moreover, since the biological treatment of high concentrations of VOCs might cause a limitation of the oxygen available for the aerobic degradation due to the reduced water-solubility of this compound, the synergic activity of microalgae and bacteria represents an efficient alternative to support the simultaneous abatement of CO_2 and VOCs. In algal-bacterial photo-bioreactors, microalgae produce oxygen during the photosynthetic process in the presence of light and CO_2, while heterotrophic bacteria utilize the additional O_2 supply to accelerate the oxidation of organic compounds. In turn, the CO_2 resulting from the mineralization process is

fixed by the microalgae. Mechanisms underlying microalgae activity might not only prevent oxygen limitation but also enhance the biodegradability of the target VOC. In this context is framed the research activity discussed in the present work, aimed to:

- the comparative evaluation of UV-assisted ozonation and its combination with conventional processes in different operating conditions;
- the comparative evaluation of two different biological reactors and the assessment of their continuous toluene degradation performances under different operating conditions;
- the scale-up of the proposed systems and the assessment of the technical feasibility.

To this end, experimental activity was structured in two main steps:

- the first one was focused on the assessment of ozone and photolysis effectiveness in promoting toluene degradation;
- the second part was focused on the assessment of enhanced biological processes for the continuous removal of gaseous toluene.

The first part of the research, focused on the comparative assessment of different configuration of AOPs systems, was performed at the Sanitary Environmental Engineering division (SEED) of Salerno University. Toluene was identified as target compound for the experimental activities. A lab-scale UV/O_3 reactor was investigated for the degradation of VOCs emissions under different operating conditions, in order to highlight the influence of the inlet concentrations and the ozone dosages. A novel configuration with an additional scrubbing phase is proposed and assessed to improve the removal efficiency and to prevent the release of polluting intermediates of the single-step process. The combined system boosted higher performance and stability compared to the stand-alone (UV/O_3) process along with a more economical and environmental sustainability.

In the second phase, the experimental activity was performed at the Department of Chemical Engineering and Environmental Technology of Valladolid University. The experimental activity aimed at evaluating and systematically comparing the continuous toluene degradation performance of the proposed biological reactors, a conventional bacterial Biotrickilng Filter (BTF) and an innovative Tubular Photo-BioReactor (TPBR). Different operating conditions have been investigated, varying the Empty Bed Residence Time (EBRT) and the toluene inlet concentration to gradually increase the Inlet Load (IL) entering the systems. Toluene mass transfer tests have been carried out in order to determine the limiting stage, and a final

robustness test performed to assess the capacity of the systems to face inlet load fluctuations.

The results obtained demonstrated the potential of the synergic effects between bacteria and microalgae. The higher DO concentrations ensured oxygen availability for the microbial community and improved the process performances. The carbon dioxide released from mineralization process was utilized for the valuable biomass production.

Conventional processes with AOPs pretreatment and microalgae-bacteria consortium inoculation thus represent innovative and promising methods for the increase of treatment efficiencies, biomass valorization and GHGs reduction.

The combination of conventional and advanced processes represents a sustainable platform to reduce the emission of undesirable byproducts, besides treating high concentrations of VOCs.

Sommario

Negli ultimi decenni, l'inquinamento atmosferico è diventato un problema sempre più allarmante, a causa degli effetti negativi registrati anche a scala globale. In tale contesto, le emissioni di gas a effetto serra (Green House Gases, GHGs), composti organici volatili (Volatile Organic Compounds, VOCs) e odori provenienti da impianti chimici, petrolchimici e altre fonti pericolose rappresentano una grande sfida da affrontare.

Il riscaldamento globale, a causa dell'aumento dei livelli di GHG nell'atmosfera, è stato identificato, infatti, come una delle sfide chiave di questo secolo. Gli impatti negativi correlati hanno causato, infatti, evidenti cambiamenti climatici e gravi danni agli ecosistemi ambientali.

I VOCs sono inclusi tra i contaminanti gassosi prioritari, ed in particolare i BTEX (Benzene, Toluene, Etilene e Xylene) sono stati identificati come il gruppo di sostanze tra i più pericolosi per la salute umana. Tali composti sono anche considerati responsabili di inquinamento fotochimico a causa della loro reazione nell'atmosfera con gli ossidi di azoto in presenza di radiazione solare. Inoltre, la loro tendenza a volatilizzarsi prontamente nell'atmosfera determina problemi di impatto odorigeno.

La combinazione di tali aspetti si è tradotta nella definizione di riferimenti normativi sempre più rigidi che, di conseguenza, hanno rafforzato la necessità di gestire correttamente le emissioni in atmosfera.

I processi chimico-fisici convenzionali prevedono il trasferimento dei contaminanti dalla fase gassosa a quella liquida e/o solida determinando, quindi, la necessità di ulteriori trattamenti. I processi biologici ed i processi ad ossidazione avanzata (Advanced Oxidation Processes, AOPs), invece, sono in grado di supportare la degradazione e la mineralizzazione dei composti organici. Inoltre, gli AOPs applicati come pretrattamento alle biotecnologie possono migliorare la trattabilità biologica dei VOCs e controllare l'accumulo di biomassa.

I processi di trattamento biologico, per elevate concentrazioni di VOCs in ingresso, potrebbero risultare limitati dall'ossigeno disponibile per la degradazione aerobica, a causa della ridotta solubilità in acqua di tali composti. In tale contesto, l'attività sinergica di un consorzio di microalghe e batteri rappresenta un'alternativa efficiente per supportare la simultanea riduzione di CO_2 e VOCs. Nei foto-bioreattori algali le

microalghe producono ossigeno durante il processo fotosintetico, in presenza di luce e CO_2, mentre i batteri eterotrofi utilizzano l'ulteriore apporto di ossigeno per accelerare l'ossidazione dei composti organici. La CO_2 risultante dal processo di mineralizzazione è fissata, dunque, dalle microalghe, con conseguente produzione di biomassa valorizzabile. I meccanismi alla base dell'attività algale possono consentire, dunque, non solo di prevenire la limitazione di ossigeno, ma anche di migliorare la biodegradabilità dei composti target.
In questo contesto viene inquadrata l'attività di ricerca discussa nel presente lavoro, che si pone come principali obiettivi realizzativi:

- la valutazione comparativa dell'ozonizzazione assistita da raggi UV e la sua combinazione con processi convenzionali, in differenti condizioni operative;
- la valutazione comparativa di due differenti reattori biologici in relazione alle loro performance di degradazione in continuo del toluene, in differenti condizioni operative;
- lo scale-up dei sistemi proposti e la valutazione della fattibilità tecnica.

A tal fine, l'attività sperimentale è stata strutturata in due fasi principali:

- la valutazione delle efficienze dei processi ad ossidazione avanzata per la degradazione del toluene;
- la valutazione dei processi biologici per la rimozione in continuo del toluene.

La prima parte della ricerca, incentrata sulla valutazione comparativa di differenti configurazioni di sistemi AOPs, è stata svolta presso il Laboratorio di Ingegneria Sanitaria Ambientale (SEED) dell'Università di Salerno. Il toluene è stato identificato come composto target. Un reattore UV/O_3 è stato realizzato e testato in laboratorio per la valutazione delle performance di degradazione in diverse condizioni operative, al fine di definire l'influenza delle concentrazioni di contaminante in ingresso e delle dosi di ozono. Il processo convenzionale è stato integrato con un post-trattamento di wet-scrubbing, per migliorare l'efficienza di rimozione e per ridurre il rilascio di sostanze gassose intermedie.
Il sistema combinato ha mostrato migliori prestazioni e maggiore stabilità di processo rispetto al sistema stand-alone (UV/O_3), nonché ridotti consumi energetici e minore rilascio di sostanze inquinanti.
Nella seconda fase, l'attività sperimentale è stata svolta presso il Dipartimento di Ingegneria Chimica e Tecnologia Ambientale dell'Università di Valladolid. L'attività sperimentale ha mirato a valutare e confrontare sistematicamente le prestazioni di degradazione in continuo del toluene dei reattori biologici proposti, un convenzionale biotrickilng filter (BTF) ed un innovativo foto-bioreattore tubolare (Tubular Photo-BioReactor, TPBR).

Sono state studiate diverse condizioni operative, al variare del tempo di residenza a letto vuoto (Empty-Bed Residence Time, EBRT) e della concentrazione di toluene in ingresso. In particolare, il carico in ingresso (Inlet Load, IL) ai sistemi è risultato gradualmente incrementato. Sono stati effettuati test di trasferimento di massa per determinare la fase limitante dei processi e un test di robustezza finale eseguito per valutare la capacità dei sistemi di sopperire alle fluttuazioni del carico in ingresso.

I risultati ottenuti hanno dimostrato il potenziale applicativo relativo agli effetti sinergici che vengono ad instaurarsi tra batteri e microalghe. Le maggiori concentrazioni di ossigeno disciolto hanno assicurato la disponibilità dell’ossigeno necessario per i processi ossidativi ad opera della comunità microbica e migliorato le prestazioni del processo. Il biossido di carbonio rilasciato dal processo di mineralizzazione dei composti organici è stato utilizzato come fonte di carbonio per produzione di biomassa valorizzabile.

I processi convenzionali con pretrattamento AOPs e la sinergia tra microalghe e batteri possono rappresentare, dunque, soluzioni innovative efficaci per l’incremento delle efficienze di trattamento, la valorizzazione di biomassa e la riduzione delle emissioni di gas climalteranti.

Acknowledgments

At the end of this PhD project, I would like to express my gratitude to all the people who help me to make this achievement come true.

First, I want to thank my tutors, prof. Vincenzo Naddeo and prof. Vincenzo Belgiorno, for all they taught me, for their meaningful suggestions and for giving me the possibility to conduct this worthwhile growth path.

I want also to express a deep gratitude to all the members of the "VOC and Odours Group" at Department of Chemical Engineering and Environmental Technology of Valladolid University, and in particular to Raúl Muñoz and Raquel Lebrero for giving me the opportunity to carry out with them part of my thesis and to learn a lot from their precious expertise and valuable suggestions. I want also to gratefully thank dr. Elisa Rodríguez and dr. Sara Turiel, which carried out the microalgae population and microbial community analysis reported in this thesis. I would also like to extend my thanks to Roxana, for her support during all my staying in the lab, and to all the others colleagues for making my research stay in Valladolid very pleasant.

I am also very grateful to dr. Tiziano Zarra for his meaningful scientific and technical support to the research activities and for sharing his knowledge with me. A special thanks goes to Paolo Napodano, who helped me to realize my experimental set-ups and to turn every laboratory misadventure in a funny moment.

I have been very lucky to have shared my doctoral period with my SEED colleagues, talented scientists and special women who have become real friends for me. In particular, I owe a lots to my "marvellous" colleagues and even more special friends Angela and Anna C., for helping me to balance my mood changes, for being always by my side.

All my fulfilments have been realized thanks to my family. My parents and my brother are a unique source of strength for me and I have to mention the essential encouragements and the unconditional, endless help they gave me in every moments of my life, any path I glide.

Lastly, thanks go to my hubby for taking loving care of me, always, and for pushing me to become stronger, the best part of myself.

ABOUT THE AUTHOR

Giusy Oliva got her Master Degree in Environmental Engineering, with honours, in 2014, discussing a thesis entitled "WEEE mechanical treatment: selection efficiency and recovery potential". In 2015 she was admitted to the Ph. D. program in Environmental and Civil Engineering at the Department of Civil Engineering of Salerno University.

Her research interest has been focused on the removal of odours and VOCs emissions by advanced processes. In 2017, she spent four months as visiting researcher at Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain).

She has been co-advisors of 10+ BSc and MSc theses. She is co-author of several papers published in international journals and congress proceedings. Currently, she is involved in initiatives promoted by SEED (Sanitary Environmental Engineering Division), at Salerno University.

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1. Introduction

In the last decades, atmospheric pollution has become an increasingly alarming problem due to its adverse effects at a global, regional and local scale, resulting in global warming, stratospheric O_3 depletion, ground level O_3 formation or acid rain among others (Mohammad et al., 2007; Paca et al., 2007; Rahul et al., 2013).

In this context, the emissions of volatile organic compounds (VOCs) and odours from chemical manufacturing plants, petrochemical industry and other industrial sources pose a major challenge due to their detrimental effects on the environment and human health (Hsu et al., 2007; Mudliar et al., 2010).

VOCs emissions have thus become a key environmental concern (Rahmani et al., 2014; Sun et al., 2012; Tokumura et al., 2012a; Zhan et al., 2018a). Extended human exposure to VOCs emissions (e.g., aromatic substances and aldehydes) may cause various health problems such as digestive, kidney, cardiac, and nervous disorders when ingested, in contact with the skin or inhaled (Franco et al., 2012). Volatile aromatic hydrocarbons, including Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) are classified as toxic, mutagenic, and carcinogenic (Gallastegui et al., 2011; Kim et al., 2014; Z. Wang et al., 2013a).

Due to these characteristics (Rahul and Balomajumder, 2013, Garoma, 2008), VOCs are included among the priority gas organic compounds, with BTEX ranking 78 from 275 substances identified as the most dangerous for human health (Akmirza et al., 2017a; Robledo-Ortíz et al., 2011).

In the atmosphere, solar radiation triggers VOCs to react with nitrogen oxides, causing photochemical smog and pollution (Franco et al., 2012; Z. Wang et al., 2013a; Ye and Ariya, 2015). For their high volatility, VOC emissions from different industrial sectors are also responsible for odour annoyance among the exposed population. Since that, odour management is becoming a prior issue for industrial operator with a view at complying with regulations and avoiding complaints from resident population (X. Q. Wang et al., 2013; Zarra et al., 2012). Petrochemical industry, plants involving paints, adhesives, solvents production, printing operations, as well as waste and wastewater treatment plants are among the main sources of anthropogenic emissions of BTEX (Carabineiro et al., 2015; Huang et al., 2016a; Kumar et al., 2008).

Furthermore, the volatile nature of VOCs often leads to odour-related problems in the nearby population, thus challenging the acceptability of existing plants and the localization of new ones (Mohammad et al., 2007; Zarra et al., 2016).

The toxicity and carcinogenicity of these compounds to human health, along with the abovementioned related problems, has triggered the enforcement of more stricter regulations, which requires the development of cost-effective and environmentally friendly technologies (Z. Wang et al., 2013b).

The more stringent regulations on air pollution and the higher expectation of the population about air quality trigger the need for the effective management and treatment of these compounds.

In this view, the scientific community have focused the attention on the development of innovative solutions for their abatement (Lebrero et al., 2014; Xu et al., 2016).

The abatement techniques currently applied for the VOC emissions treatment involves activated carbon adsorption, absorption, biofiltration and thermal or catalytic combustion (C. Y. H. Chao et al., 2007; Liang et al., 2013; Ch. Subrahmanyam et al., 2010). The drawbacks of these conventional solutions include contaminant transfer to other phases, inefficient biological treatments due to load fluctuations and presence of recalcitrant and toxic secondary metabolites (C. Y H Chao et al., 2007; C. Subrahmanyam et al., 2010; Vergara-Fernández et al., 2007).

To overcome the limitations of the conventional processes, numerous researches are focused on Advanced Oxidation Processes (AOPs) for the abatement of gaseous VOCs.

These processes rely on the effects of hydroxyl radicals, highly reactive oxidants, able to degrade a wide-range of organic compounds (Johnson et al., 2014a; G. Liu et al., 2017; Vega et al., 2014; Yao et al., 2014).

Among them, ozonation supported by ultraviolet irradiation (UV/O_3) is a promising method to degrade recalcitrant and hydrophobic VOCs (Z. W. Cheng et al., 2013). Ozone enhanced the degradation capability of the combined process not only due to its high oxidation potential, but also by the formation of strong oxidants such as hydroxyl and oxide radicals (Z. W. Cheng et al., 2013).

Ozone was produced by the irradiation of air with the UV lamps. The photolysis/irradiation of ozone then leads to the hydroxyl radicals formation (Jeong et al., 2005).

The presence of water vapor irradiated with UV also generate additional radicals (Johnson et al., 2014a). However, the further irradiation of ozone lead to the greater contribution of hydroxyl radicals.

Different studies evaluated the performances of toluene oxidation by UV/O_3, varying different operational parameters, including inlet concentration, ozone concentration, gas flow rate and humidity, using UV lamps and separate ozone generators (Pengyi et al., 2003a; K. P. Yu and Lee, 2007).

These studies suggested that the UV/O_3 process is a suitable technology with the aim at degrading toluene. The main disadvantage of the application of UV/O_3 treatment is the formation of undesirable by-products resulting from the UV irradiation and ozone oxidation (Zhan et al., 2018a).

Since most of the by-products formed by toluene oxidation have high water solubility, the integration with a conventional air bubble wet scrubbing supported a synergic effect. The water-scrubbing step allowed to overcome the main limitation of the stand-alone system, mainly concerning the release of undesirable by-products into the atmosphere and the high energy consumption (Akmirza et al., 2017b; Moussavi and Mohseni, 2007).

Even if physical-chemical treatment technologies represent widely used platforms for the removal of toluene (Akmirza et al., 2017a; Chen et al., 2010a), their application for the abatement of VOCs-laden off-gases characterized by high flow rates and relatively low VOCs concentrations (less than 100 ppm), is not economically feasible as a result of their large consumptions of chemicals and energy (Lebrero et al., 2016a; Schiavon et al., 2016).

Biological processes have become mature and low-cost alternatives to physical-chemical treatment technologies for VOCs degradation (Chen et al., 2010a; Malakar et al., 2017). Biotrickling filters (BTFs) exhibit clear advantages over the rest of biotechnologies, including (i) better process stability and control of the operating parameters thanks to the continuous trickling of an aqueous nutrient solution, and (ii) reduced operating costs (Lebrero et al., 2012; Mudliar et al., 2010). On the contrary, the treatment of high concentrations of VOCs in BTFs typically causes biomass overgrowth (which ultimately results in packing media clogging), process inhibition due to acidification of the cultivation broth, and a limitation of the oxygen available for the aerobic VOC degradation due to the reduced water-solubility of this compound.

In this context, the synergisms between microalgae and bacteria in suspended-growth photo-bioreactors represent an efficient alternative to prevent O_2 limitation, acidification and biomass overgrowth operational problems during VOCs biodegradation.

In algal-bacterial photo-bioreactors, microalgae produce oxygen during the photosynthetic process in the presence of light and CO_2, while heterotrophic bacteria utilize this additional O_2 supply to accelerate the oxidation of VOCs. In turn, the CO_2 resulting from VOC mineralization is photosynthetically fixed by microalgae with a concomitant rise in the pH of the cultivation medium. Furthermore, microalgal activity might not only prevent oxygen limitation but also enhance the biodegradability of the target VOC (Lebrero et al., 2016a).

Despite their advantages, the number of studies exploring the merits of algal-bacterial photo-bioreactors for VOCs removal is scarce and a better understanding of the microbial communities and their interactions within the algal-bacterial consortia is necessary.

1.1 Objectives

According to what previously reported, the overall aim of this Ph.D. research project is the identification of innovative solutions for the advanced treatment of waste gas contaminated by odours and VOCs.

To this end, a comparative study of current abatement technologies towards innovative solutions for the control of the target compounds was carried out.

In particular, the experimental activity was structured in two main section:

- the first section aims at evaluating the VOCs degradation performance by UV-assisted ozone oxidation (UV/O_3) and comparing the stand-alone process to the hybrid system with an additional wet scrubbing step (UV/O_3+S). The influence of contaminants inlet concentration and applied voltage on the removal of toluene was analyzed to define and evaluate the performances of the investigated systems;
- the second section aims at evaluating and systematically comparing the continuous toluene abatement performance of a conventional bacterial BTF and an innovative tubular algal-bacterial photo-bioreactor (TPBR). The influence of the empty bed residence time (EBRT) and the toluene inlet concentration on pollutant biodegradation was investigated in both bioreactors. Toluene mass transfer tests were carried out in order to determine the limiting stage under the multiple operational conditions evaluated, and a final robustness test was performed to assess the capacity of the bioreactors to cope with toluene surges. The dynamics of the microbial communities in both bioreactors were also determined using molecular biology techniques.

To this extent, a literature review on current technologies and emerging processes for wastegas treatments as well as their combination in hybrid systems was undertaken in order to gather background information and define the experimental activity.

Four different experimental setups have designed and constructed. Among VOCs, toluene was selected as model compound, due to its widespread presence in various industrial exhaust emissions, in order to create a simplified model by the use of a synthetic gaseous stream (Ahmadi et al., 2017; G. Liu et al., 2017; Xu et al., 2016). To achieve the set objectives, the following aspects have been investigated:

- the overall treatment performance of the proposed systems, evaluating, in particular, the influence of the toluene inlet load and resident time;
- the influence, in the AOPs systems, of the applied voltage on the release of by-products and the optimization of the process with a wet scrubbing as down-stream treatment;
- the influence, in the bioreactors, of operating parameters on the presence of secondary metabolites which may cause process deterioration;
- the influence, in suspended-growth photo-bioreactor, of the microalgae consortium activity on the dissolved oxygen concentration in liquid phase and algal biomass production.

1.2 Outlines

The research activity performed in the Ph.D. period follows an in-depth analysis of scientific literature background.

In Chapter 2 are reported the characteristics of the identified target compounds, odours and VOCs, which a view at pointing out the importance of their effective management.

The Chapter 3 describes the current physical, chemical and biological technologies applied for waste gas treatment, highlighting the main aspects, the possible configurations, weakness and straights points, the performance potential as well as the current status of their application, with particular reference to VOCs removal.

Main AOPs treatment technologies, applied as emerging solutions for waste gas treatment, are overviewed in the Chapter 4. Both single-stage process and hybrid systems have been proposed in the technical-scientific community and reported in the above-mentioned chapter, by focusing on the basic action mechanisms of hydroxyl radicals formation and on the influence of contaminants characteristics and operating conditions for the process sustainability.

The possibility to exploit photosynthesis-based technologies for the simultaneous CO_2 fixation and VOCs removal is extensively discussed in Chapter 5, with particular regards to the merits of microalgae cultivation and photo-bioreactor configuration.

Chapter 6 illustrates the investigation plan and the single stages in which it has been organized the experimental activity.

In Chapter 7, experimental setups, sampling and analytical methods are illustrated with reference to the experimental research activity, organized in the following phases:

- design and construction of the UV/O_3 system at pilot scale;
- integration of wet scrubbing process as a down-stream process into the single-stage ozonation process (hybrid UV/O_3+S);
- realization of experimental tests, in triplicate, to systematically evaluate the performance of the systems toward removal efficiency and by-products formation;
- design and construction of the conventional BTF and the innovative photo-bioreactor (TPBR) at pilot scale;
- evaluation of the continuous toluene removal with BTF and TPBR, under different operating conditions;
- evaluation of the CO_2 fixation, biomass production and in TPBR.

The first three phases were conducted at the Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering of Salerno University (Italy). The last third phases were performed for four months at Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain). Chapter 8 shows the results and discussion of the overall experimental activity. Concluding remarks and future perspectives are presented in the Chapter 9.

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2. Emissions of odours and gas pollutans

The exposure to VOCs has been related both to acute symptoms such as nausea, headaches, loss of consciousness and to chronic effect associated to mutagenicity and carcinogenicity risks (Son, 2017).

The formation of ozone and PAN (Peroxy Acetyl Nitrate) could be also triggered by the emission of VOCs (Parmar and Rao, 2008). Along with these effects, the correlated odour emissions may cause annoyance and discomfort to the exposed people (Naddeo et al., 2016).

Exposure to environmental odour indeed can result in annoyance, health effects and depreciation of property values.

Odour has been identified as an atmospheric pollutant and, among them, it represents the major cause of complaints from citizens to local authorities in many different contexts (Capelli and Sironi, 2018; Henshaw et al., 2006). Odour pollution is nowadays a serious hindrance and thus is currently subjected to specific regulation in many countries (Capelli et al., 2013; Loriato et al., n.d.).

The existence of regulatory acceptability criteria entails the necessity to develop suitable methods for odour impact assessment and control.

Based on these evidences, the necessity to correctly manage VOCs and odour emissions is of key importance.

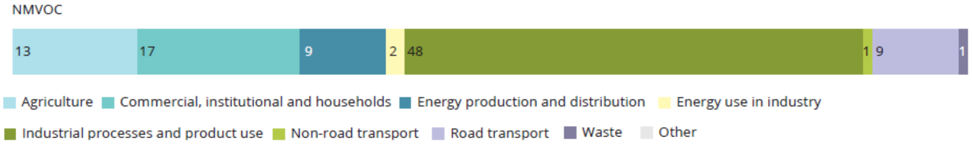
2.1 Volatile organic compounds

Volatile organic compounds (VOCs) are defined as carbon-containing compounds that participates in atmospheric photochemical reactions. Most VOCs are very short-lived in the atmosphere and have an impact as ozone generating substances, entailing also serious occupational health effects.

The definition of VOCs may vary from the authors, but the general characters are the low boiling point, high vapour pressure and strong reactivity towards photochemical reactions. VOCs are emitted both from anthropogenic and natural sources. The main attention it should be paid for the significant increase of anthropogenic emissions due to the development of the industrial sector.

Since VOCs consist of chemical species which may be related to the increase in tropospheric ozone concentrations and the formation of secondary organic aerosols, numerous Regulation have been displayed including the Directive on ambient air quality and cleaner air for Europe (2008/50/EC), the industrial emissions Directive (2010/75/EU) and the deco-paint Directive (2004/42/EC).

In Figure 2-1 are reported the contribution of each sector to the emissions of NMVOCs (Non-Methane VOCs). Industrial processes and product use are the main contributor to the NMVOC emissions. Among European Countries, the largest emitter of NMVOCs in 2016 was Germany, followed by Italy and the United Kingdom. Between 2015 and 2016, 16 Member States reported emission reductions for NMVOCs.



Sources: EEA, 2018c, 2018e.

Figure 2-1: Contribution to EU-28 emissions from main source sectors in 2016 of NMVOCs (adapted from Guerreiro et al., 2018)

Benzene, toluene, ethylbenzene, o-, m- and p-xylene (BTEX) are aromatic VOCs. Among these, Benzene is classified in Group 1 (human carcinogen) by the International Agency for Research on Cancer. Toluene, ethylbenzene, o-, m-, and p-xylenes have been found to be cause of adverse health impacts with respiratory and neurological effects (Zhang et al., 2017).

In Table 2-1, it has been reported an overview of the Sources and health effects of major VOCs.

Table 2-1: Sources and health effects of major VOCs (adapted from Zhang et al., 2017)

Classification	Representatives	IDLH* [ppm]	Sources	Health effects
Alcohols	Methanol Ethyl alcohol Isopropyl alcohol	6000 3300 2000	Antiseptics Preservative Cosmetics and personal care products	Throat irritation and shortness of breath Eye irritation Central nervous system depression
Aldehydes	Formaldehyde Acetaldehyde	20 2000	Decorative and construction materials Cosmetics and plastic adhesives Fabrics and bio-waste decomposition Biomass burning Degradation of VOCs in multiple steps oxidations	Irritation of the throat, eyes and skin Nasal tumors Predecessor of ozone
Alkenes	Propylene Ethylene	-	Petrochemical syntheses Production of varnishes Synthetic resins, adhesives, printing ink Organic intermediates of pharmaceutical and perfumes	Photochemical ozone creativity potential Potentially carcinogenic and adversely affects the odor and taste of drinking water
Aromatic compounds	Benzene Toluene Ethylbenzene	500 500 800	Petroleum products Incomplete combustion of liquid fuels Adhesives Lacquers	Carcinogen Damage the ozone layer Produce photochemical smog, and pose mutagenic hazards
Halogenated VOCs	Carbon tetrachloride Chlorobenzene Trichloroethane Tetrachloroethane Trichloroethylene Tetrachloroethylene Dichloromethane	200 1000 100 100 1000 150	Chemical extractant Paints Adhesives Polymer syntheses Water purification systems	Strong bioaccumulation potential Acute toxicity Destruction of the ozone Cause greenhouse gas effects
Ketones	Acetone Ethyl butyl ketone	2500 1000	Varnishes, window cleaners, paint thinners, adhesives	Irritation of eyes, nose, and throat Central nervous system depression
Polycyclic aromatic hydrocarbons	Phenanthrene Pyrene	-	Release from creosote and incomplete combustion of organic matter, coal, oil, and biofuels	Carcinogen

Most VOCs, including aldehydes, aromatic compounds, polycyclic aromatic hydrocarbons, alcohols and ketones are highly toxic and carcinogenic.

The most widespread VOCs in indoor environment are aldehydes, especially formaldehyde and acetaldehyde present in furniture and building materials. These compounds are related to chronic toxicity as well as nasal tumours for high concentrations.

The exposure at low concentration of aromatic compounds would induce confusion, tiredness, nausea and general disease, loss of appetite, memory and sight. For high concentration, the inhalation may cause unconsciousness, dizziness, and even death. In particular, benzene cause leukaemia and lymphomas; at 2% of benzene in air 5–10 min of exposure may be fatal.

Polycyclic aromatic hydrocarbons (PAHs) contain benzene rings and include naphthalene, phenanthrene and pyrene, identified as carcinogenic VOCs. Ethanol, isopropanol and n-butanol have been found to affect nervous system.

Along with the well-known effects and damages on human health, VOCs are identified as major contributors to stratospheric ozone depletion. Indeed, VOCs can reach the stratosphere, resisting at the oxidation processes, photolysis, physical removal, reaction with atmospheric hydroxyl free and ozone, which take place in tropospheric removal processes. Moreover, halogenated VOCs can participate in the stratospheric photolysis and, consequently, release active ozone-destroying chain carriers.

The volatile nature of these compounds also often entails odour-related problems in the surrounding of VOCs industrial sources. Even if the VOCs emissions comply with the Regulation and the concentration levels are acceptable for human health, the emission of VOCs at trace level could also determine odour annoyance.

2.2 Odours

Odour can be defined as a sensation resulting from the interaction of volatile chemical species inhaled through the nose, including volatile organic compounds (e.g. esters, acids, aldehydes, ketones, alcohols) (Brancher et al., 2017).

In particular, the environmental odours emitted from anthropogenic sources derived mainly from industrial and agricultural activities, waste and wastewater treatment plants, food industry, rendering plants, landfills, livestock buildings, foundries, petrochemical parks, slaughterhouses, paper and pulp facilities, composting activities (Leonardos et al., 1969).

The odorant may interact with receptors in a negative fashion, causing an impact which often results in complaints. In this context, it is essential the statement of

Regulations about odour pollution to address the resolution of conflicts. The complaints, indeed, arise from odour annoyances, adverse effects on human health and price depreciation of properties (Brancher et al., 2017).

However, the complexity of odour compounds, along with the still scarce know-how about the relationship between olfactory value and odour families and identification of the principal odorants are the key factors that limited a shared approach for the odour Regulations (Cheng et al., 2019).

The problems related to the long term exposure to odorant pollutants (e.g., benzene, toluene, xylenes, benzene chloride, etc.) result in adverse effects on human health (Davoli et al., 2010; Durmusoglu et al., 2010; Nadal et al., 2009) since are associated to non-carcinogenic or carcinogenic risks. In particular, ethylbenzene in odour nuisance is recognized as dominant health threat compound (Cheng et al., 2019; Yanjun Liu et al., 2016).

With a view at addressing suitable strategies for odour and air pollution abatement, the characterization of volatile compounds responsible for malodours and environmental hazards is of key importance (Rincón et al., 2019). The factors that influences environmental odour impacts were described in terms of frequency, intensity, duration, offensiveness and location (FIDOL factors).

The FIDOL factors influence the extent to which odours adversely affect communities and this information can be used as a basis for conducting odour impact assessment studies (Nicell, 2009).

The frequency is expressed by a percentile (P), which state the permitted number of exceedances of a specific odour concentration threshold. The duration is related to the elapsed time during which an odour occurs. The offensiveness describes the odour character, by means of hedonic tone. The location is related to the land use in the surrounding area of an odour source, taking into account socioeconomic, tolerance and expectation issues (Brancher et al., 2017; DEFRA, 2010).

The odorous gas samples concentrations are mainly characterized either by analytical and sensory methods (Capelli et al., 2008; Ueno et al., 2009).

The most implemented sensory method is Dynamic Olfactometry (DO), used in Europe to measure the Odour Concentration (OC) expressed in OU_E m^{-3} (Laor et al., 2014). OC measurement is realized by diluting a gas sample with odourless air to determine the dilution factor, which corresponds to the condition in which 50% of a calibrated human panel can perceive an odour stimulus. Since it is based on the responses of a human panel, this technique is considered among the most appropriate method to characterize the odours released to the atmosphere. Indeed, odour Regulations in different countries are based on the definition of odour concentration and its standards are reported in UNI:EN 13725:2003 (Blanco-Rodríguez et al., 2018; Brancher et al., 2017; Rincón et al., 2019).

However, DO is expensive, time-consuming and presents lower repeatability and accuracy due to its subjective nature (Brattoli et al., 2011).

On the other hand, analytical methods are based on the evaluation and quantification of the chemical composition by instrumental-based techniques such as GC/MS, gas tubes and wet methods (scrubbers and traps) (Blanes-Vidal et al., 2009; Blazy et al., 2015; Tsai et al., 2008).

The principal advantage of using instrumental methods is the difficulty to determine odour contributors from complex gas mixtures of volatile compounds (Gallego et al., 2012), relating the compounds with their corresponding Odour Detection Thresholds (ODTs) (Rincón et al., 2019). In particular, ODT is defined as the compounds chemical concentration at which 50% of the panellists can perceive the olfactory stimulus (Capelli et al., 2009) and the ratio between the chemical concentration of a single compound to its ODT is defined as odor activity value (OAV). OAV is a widely employed parameter for the monitoring of odorants in composting gas emission (Blazy et al., 2015; Fang et al., 2013; Schiavon et al., 2017; Yan-li Zhu et al., 2016). However, deriving odour concentration with this exhibits two main disadvantages: i) the considerable variability among ODTs found in the literature and ii) the fact that interactions among odorous molecules which may produce synergistic, antagonistic or even neutralizing effect are not take into consideration (Wu et al., 2015).

In that view, to overcome the limitation of sensory and instrumental methods, in the last years the proposition of sensorial-instrumental technique is rapidly expanding (Yan et al., 2015).

Electronic nose represents indeed an attractive tool for the monitoring of environmental odours, with a view at obtaining real-time information, to support the decision-making process and for the implementation of proactive approaches (Biolatto et al., 2007; Scott et al., 2006).

The use of electronic devices for odour monitoring purposes is of key interest since they offer the strengths of both sensorial and analytical instruments and the opportunity to detect odour concentration and odour quality.

Nowadays, among the most challenging problems related to the application of e-nose, the adequate selection of the sensors array for the specific application, with high robustness, selectivity and reproducibility, assumes a key role (Blanco-Rodríguez et al., 2018; Wang et al., 2019).

Moreover, the needs to face with the complexity of gaseous mixtures from industrial sources, boosted the attention given to sampling technique, training phase and data analysis. These activities have to be adapted to the specific requirements. In particular, the attention paid for data processing resulted in different possibilities to implement, among which emerged statistical pattern recognition, artificial neural networks, chemometrics, machine learning (Fu et al., 2007; Tao et al., 2008).

The rising number of e.Nose real applications in different industrial sectors have triggered the enhancement of these systems to overcome their main drawbacks. The availability of more detailed information about the genetics behind the olfactory receptors, along with the increasing awareness regarding the relations between odorants molecular properties and the odour offensiveness should be deeply investigated in order to increase the representativeness and the cross-sensitivities of the measurements (Boeker, 2014; Wijaya et al., 2019).

Overall, the standardization of different kind of measurements at least at European Level may represent an essential step forward in order to solve the main odour related challenges and provide advances for wider applications in different sectors. Consequently, the proposition of International Standards is strongly required (Naddeo et al., 2016, 2013).

In that view, the opportunity to merge different expertise in the sector is a strategic approach to provide useful tools for the odour emissions characterization and control. An integrated strategy can improve scientific background for the development of odour regulations, providing solid common basis for setting robust and harmonious regulatory approaches for odour impact assessment.

3. Conventional Treatment for the abatement of gas pollutants

The increase of VOCs emissions and the enforcement of stricter Regulations have triggered the identification of effective solutions for the management of VOCs emissions (Zhang et al., 2017).

The strategies implemented for the control of these emissions are aimed at (Delhoménie and Heitz, 2005):

- avoiding the use of certain VOCs in industrial processes;
- modifying existing processes to reduce their associated VOCs emissions;
- installing depollution systems downstream of the emitting sources.

In particular, this necessity forced the consolidation and emersion of depollution techniques, which can promote either recovery or destruction of the VOCs. The recovery methods include adsorption, condensation, absorption, and membrane separation, whereas destruction methods include incineration, catalytic oxidation and biological degradation. The destructive methods basically convert VOCs into carbon dioxide and water and thus do not require further treatments. On the contrary, the recovery methods may allow the materials recovery (Zhang et al., 2017).

In details, conventional technologies for the treatment of atmospheric pollutants can be mainly classified as biotechnologies and physical-chemical processes.

Figure 3-1 presents the application limits in terms of flow rates and VOCs inlet concentrations of different conventional waste gas treatment technologies.

The selection of the adequate treatment technology depends mainly on gas flow rate, pollutant inlet concentration, pollutant solubility in water and biodegradability level, temperature initial investment, operation and maintenance (Delhoménie and Heitz, 2005; Muñoz et al., 2015; Parmar and Rao, 2008; Son, 2017).

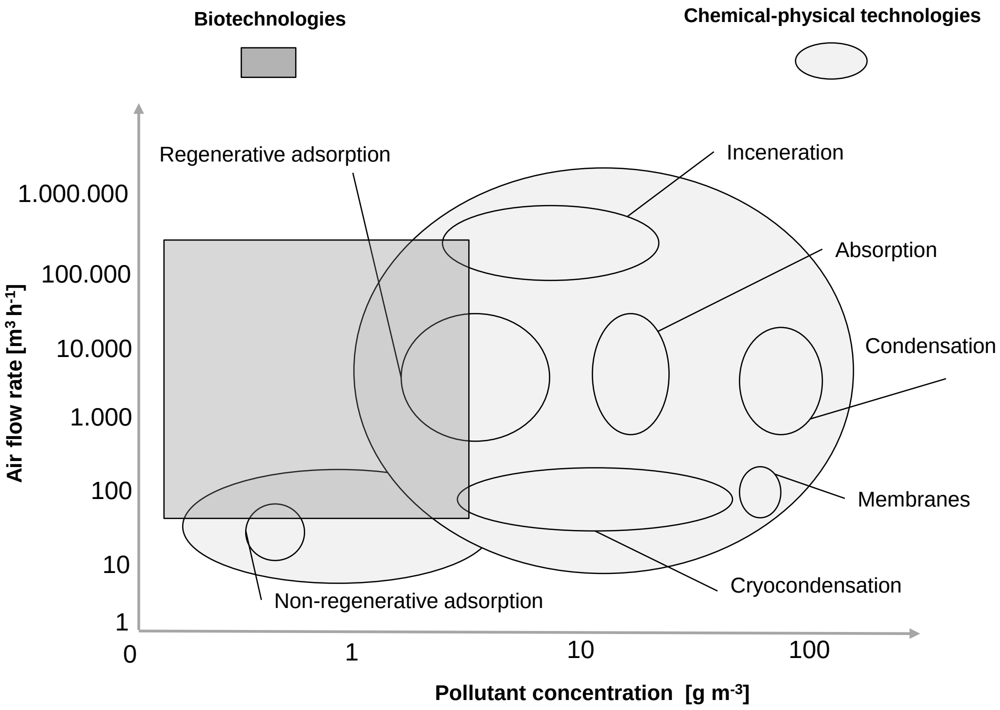


Figure 3-1: Application limits (flow rate—VOCs concentration) of different conventional waste gas treatment technologies (adapted from Muñoz et al., 2015)

Chemical-physical treatments are among the most used technologies and consequently they are characterized by an established know-how. Their application for industrial emissions, often characterized by high flowrate and low contaminant concentration, may not be economically feasible due to the large amount of energy and chemicals required (Boyjoo et al., 2017).

Biological and oxidation processes are able to promote the partial or complete degradation of organic compounds, resulting into their mineralization. Consequently, these processes do not require further treatment of the phases to which the contamination may be transferred.

Biotechnologies, despite the fact that show an effective removal with economic and environmental friendly processes, for high inlet concentration are often limited by the presence of recalcitrant and toxic secondary metabolites and the microbial activity may be inhibited by the oxygen limitation (Lebrero et al., 2016a).

The main advantages and disadvantages of the current methods for off-gas treatment are reported in Table 3-1.

Table 3-1: Characteristics of VOCs and odorous compound control technologies (Khan and Kr. Ghoshal, 2000; Parmar and Rao, 2008; Son, 2017; Son et al., n.d.).

Techniques	Annual Operating cost [USDcfm^{-1}]	Removal efficiency [%]	Secondary waste generated	Merits and demerits
Absorption	25-120	90-98	Wastewater	- Product recovery can offset annual operating costs - Requires rigorous maintenance - Requires pretreatment of the target compounds
Adsorption - Activated Carbon	10-35	80-90	Spent carbon/collected organics	- Recovery of compounds, which may offset annual operating costs - Susceptible to moisture, and some compounds (ketones, aldehydes, and esters) can clog the pores
Adsorption - Zeolite	15-40	90-96	Spent zeolite/collected organics	- Effective in more than 90% RH, Recovery of compounds offsets annual operating costs - High cost of zeolite, restricted availability
Biofiltration	15-75	60-95	Biomass	- Requires less initial investment, less non-harmful secondary waste, and nonhazardous - Slow, and specific microbes decompose organics selectively, thus requires a mixed culture of microbes
Condensation	20-120	70-85	Condensate	- Product recovery can offset annual operating costs - Requires rigorous maintenance
Catalytic Oxidation	15-90	90-98	Combustion products	- Energy recovery is possible (maximum 70%) - Efficiency is sensitive to operating conditions
Thermal Oxidation	15-150	95-99	Combustion products	- Energy recovery is possible (maximum 85%) - Halogenated and other

				compounds may require additional control equipment
Membrane separation	15-30	90-99	Exhausted membranes	- No further treatment, recovery of solvent may offset the operating costs - Membranes are rare and costly
Plasma	n.a.	90	Aerosols, Ozone, Trace gaseous compound	- This treatment especially beneficial for low concentrations of VOC and odorous compounds, has the advantage of energy saving and no production of dioxin - In general needs pretty huge electrical energy, solvents cannot be recovered for reuse
Photocatalysis	n.a.	90-100	Aerosols, Ozone, Trace gaseous compound	- Sunlight can be used to active low-cost photocatalyst - Amenable to scale-up - Wider scope of application - Reaction rates need to be enhanced 10–100 fold for cost-effectiveness

3.1 Biological treatments

Biotechnologies are considered the best option for the treatment of high flowrate characterized by relatively low inlet concentration, as also confirmed by ***Figure 3-1***.

Biological processes are based on the capability of microorganisms to convert a wide variety of gas pollutants into less toxic and odourless compounds (Muñoz et al., 2015).

The advantages of biological processes over the chemical-physical counterpart mainly consist in the fact that they can be conducted at atmospheric pressure and temperature, resulted simpler and more economical to implement, with a lower carbon footprints entailed (Estrada et al., 2011).

The microorganisms, indeed, exhibit a reliable capacity to metabolize a wide range of VOCs, promoting their biocatalytic oxidation. The heterotrophic microbial strains (bacteria, fungi) work as catalysts able to use contaminants, oxidized in the course of the catabolic pathway (respiratory chain), as source of energy and to use contaminants also as source of available carbon for the anabolic processes, such as cell growth. Biological reactions essentially produce carbon dioxide, water, inorganic by-products, new cellular matter and organic by-products (metabolites). These reactions are exothermic and, thus, also heat is released during the processes (Delhoménie and Heitz, 2005).

The critical parameters for bioreactors operation are (Muñoz et al., 2015; Shareefdeen and Singh, 2005):

- temperature (optimum between 20 and 35°C for a mesophilic microflora);
- pH (optimum at about 7);
- moisture content in the growth medium;
- availability of essential non-carbon nutrients (N, P, K, S and micronutrients).

The empty bed residence time (EBRT) is the main design parameter. The setting of EBRT influence the reactor volume, the volumetric load and, consequently, the economics of the process.

$$EBRT = \frac{V}{Q}$$

Where V and Q are the bed volume and the gas flow rate of the treatment system, respectively.

The EBRT ranges between few seconds to several minutes, depending on the characteristics of the pollutant emission (Estrada et al., 2013).

The amount of pollutant entering the treatment system is usually quantified in terms of t inlet load (IL), defined as:

$$IL = C_{in} \cdot \frac{Q}{V}$$

Where C_{in} is the pollutant concentration at the inlet of the treatment system.

The reactors performances are often assessed both in terms of elimination capacity (EC) and removal efficiency (RE).

$$EC = (C_{in} - C_{OUT}) \cdot \frac{Q}{V}$$

$$RE\ [\%] = \frac{(C_{in} - C_{OUT})}{C_{IN}}$$

Where C_{out} is the pollutant concentration at the outlet of the treatment system.

The performance of biotechnologies are mainly affected by (i) the bioreactor configuration, (ii) the selection of adequate packing materials, (iii) the microbial performance and (iv) the hydrophobicity characteristics of the gas pollutant.

3.1.1 Biofiltration

Biofilters (BFs) are bioreactors with a fixed-bed where degrading microorganisms are immobilized. They are the oldest biotechnologies configuration.

The contaminated waste gas, including pollutant vapors and oxygen, is forced to pass through the porous material. The porous media may be composed of organic (such as bark and wood chips), inorganic (such as ceramics) or synthetic materials (such as granulated carbon or plastics) (Alfonsín et al., 2015; Cheng et al., 2016).

The biological reactions take place into the biofilm, synthesized by the microflora, without a mobile liquid chase. This aspect triggers the application of BFs for the treatment of compounds poorly soluble in water.

Two possible BF configurations are implemented (Barbusinski et al., 2017):

- in open designed biofilters (Figure 3-2) waste gas has ascending flows. The upper part of the reactor is in contact with the atmosphere and, consequently, exposed to weathering, because of the large spaces required which forced outside installations;
- in enclosed biofilter (Figure 3-3), instead, ascending or descending gas flows are implementable. More restricted volumes are needed and, thus, indoor configuration are possible. Therefore, the process parameters (including fluid flow, fluid composition, and temperature) are easier to monitor and control.

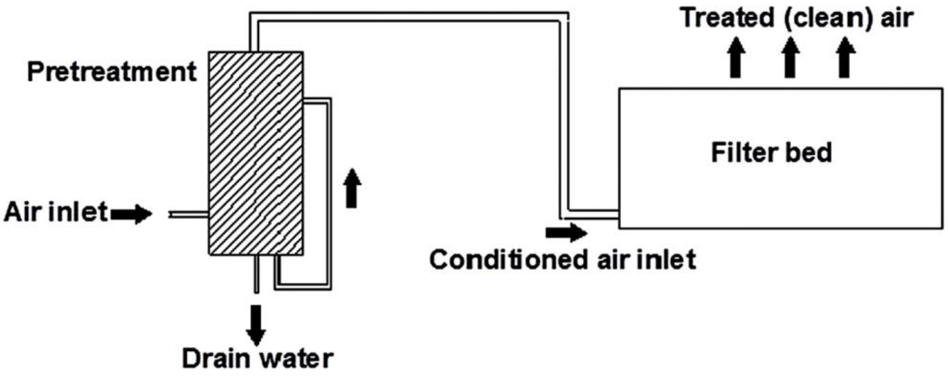


Figure 3-2: Schematic of an open biofilter (adapted from Kennes and Veiga, 2001)

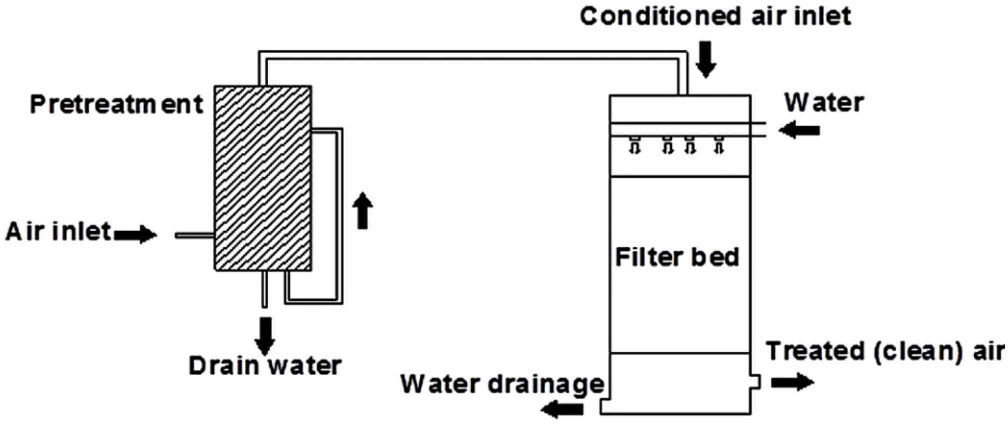


Figure 3-3: Schematic of an enclosed biofilter (adapted from Kennes and Veiga, 2001).

In Figure 3-4 it has been reported the schematization of removal processes in the biofiltration. The process takes place at biofilm level, medium level and reactor level. The biodegration occurs after the diffusion of the contaminant in the bulky gas from the gas phase to the water phase or biofilm. The diffusion depends on the mass transfer rate related to the Henry's law constant (Anderson, 1992; Vane and Giroux, 2000). Acid Metabolite are produced as a result of VOC biodegradation occurring in the biofilm. Metabolites, VOCs and oxygen are all subjected to simultaneous diffusion and adsorption within the biofilm and on the pore of packing material (Deshusses et al., 1995; Shareefdeen and Baltzis, 1994). The neutralization of the acidification due to metabolites production is often limited by the addition of limestone powder or other pH buffer agents (Smet et al., 1996; Wang et al., 2014; Yang et al., 2008).

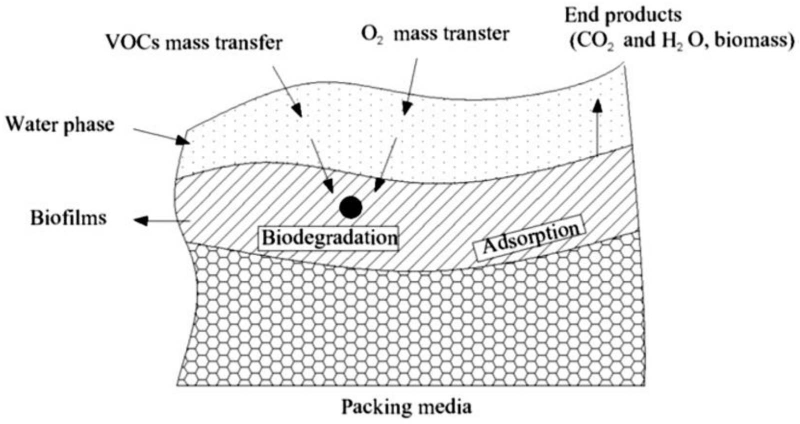


Figure 3-4: Phenomena involved in the operation of bioreactors (adapted from Cheng et al., 2016).

The waste gas is humidified before to be in contact with the biofilm which promotes the aerobic degradation, ensuring a residence time sufficient to allow the contaminants mass transfer from the gaseous phase to the biofilm (Muñoz et al., 2015).

Since the biofilm is partially covered by a water layer, good performances are supported for moderately hydrophilic pollutants, with dimensionless Henry's law constant (DHLC) between 0.1 and 0.99 (Kraakman et al., 2011). The addition of non-aqueous phase could enhance bioreactors removals for hydrophobic pollutants (Lebrero et al., 2014).

The packaging media in BFs provide the surface for the attachment and grow of microorganisms and the reservoir of water, pollutants and nutrient for microorganisms activity.

Organic packing medium make available for the microorganisms the nutrients contained in the organic residues whose they are composed of. When inorganic materials are used as packaging materials, the addition of external nutrients is mandatory (Anet et al., 2013; Gutiérrez-Acosta et al., 2012).

Even if packing material used in BF systems already contains nutrients for the growth of microorganisms, the supply of some extra nutrients may enhance the biodegradation of VOCs (Wahman et al., 2007).

The extended operation of BFs may lead to the increase of the thickness of the biofilm, especially for high inlet loads. This condition changes the porosity of biofilter bed, which gradually decreases with the increase in duration of operation, VOCs incoming loading, or by decreasing empty bed residence time (EBRT) (Devinny and Ramesh, 2005; Yang Chunping et al., 2004). Consequently the clogging of packaging material may occur because of the biomass exceeding causing excessive head loss, channel formation of gas streams within biofilters, diffusion limitation at the deeper part of the bed (Bouchaala, 2012; Wang et al., 2014).

Singh et al. (2010) evaluated the performance of a conventional biofilter packed with polyurethane foam for toluene removal: removal efficiency ranged from 68.2 to 99.9% and elimination capacity ranged from 10.85 to 90.48 g $m^{-3}h^{-1}$ were obtained.

Removal efficiencies ranging between 40 to 95% and elimination capacities from 3.5 to 128 g $m^{-3}h^{-1}$ depending on the incoming loading rates were observed by Rene et al. (2005) with a compost-based biofilter unit inoculated with a mixed microbial population.

Moreover, Zhu et al. (2016) investigated the performances of a lab-scale biofilter packed with compost, cement, perlite, $CaCO_3$, plant fiber, using sodium silicate as adhesive. Maximum elimination capacity of 36.0 g $m^{-3}h^{-1}$ were observed for an inlet loading rate of 45.9 g $m^{-3}h^{-1}$. Empty bed residence times was gradually decreased from 148.3 to 49.4 s and inlet concentration inlet concertation increased from 0.2 to 1.2 g m^{-3}; for the investigated conditions, a maximum removals yield of 95% was recorded.

The main advantages that BF systems exhibit are cost effectiveness, almost no secondary pollution, low pressure drop and the possibility to treat large volumes at low VOCs concentration.

On the contrary, the control of pH and moisture it could be difficult to carry out, the clogging of the medium due to particulate matter and excess biomass along with medium deterioration may occur. Moreover, the treatment efficacy is significantly affected by the increasing the pollutants concentrations (Wu et al., 2018).

3.1.2 Biotrickling filters

In biotrickling filters (BTFs), the waste gas passes through a packed bed filled with inert material supporting the growth of microorganisms (Figure 3-5).

The combination of different physicochemical and biological phenomena take place. The different mechanisms which occurs in BTF are shown in Figure 3-6.

The microorganisms are immobilized on the surface of the packing material and the surface of biofilms is covered by a water phase. Consequently, VOCs and odorous pollutants in the waste gas have to be first transferred to the water phase layer. The contaminants are then moved to microbial cells in the biofilm (Wu et al., 2018).

The gaseous pollutants and oxygen are transported in water phase by concentration gradient differences, by mass transfer process (Kraakman et al., 2011; Lebrero et al., 2012).

The contaminants are absorbed to the biofilm for the degradation supported by the microorganisms and used as energy source for the bacterial growth. The cellular metabolism is promoted to breaks down the chemicals into simpler and harmless compounds.

In particular, biodegradation reactions allow the assimilation of the dissolved contaminants through their conversion to CO_2 or other poorly volatile intermediates with simple chemical structures. The microorganisms utilize the energy from the oxidation reactions to form, in the presence of nutrients, a biofilm.

Eventually, carbon dioxide released by microbial degradation can be transferred to gas phase or f can form carbonate in aqueous phase (Wu et al., 2016).

The process effectiveness is thus strictly depending on the occurrence of both mass transfer from gas to biofilm and biodegradation reactions and so the process could be limited by diffusion or microbial activity (Li et al., 2012).

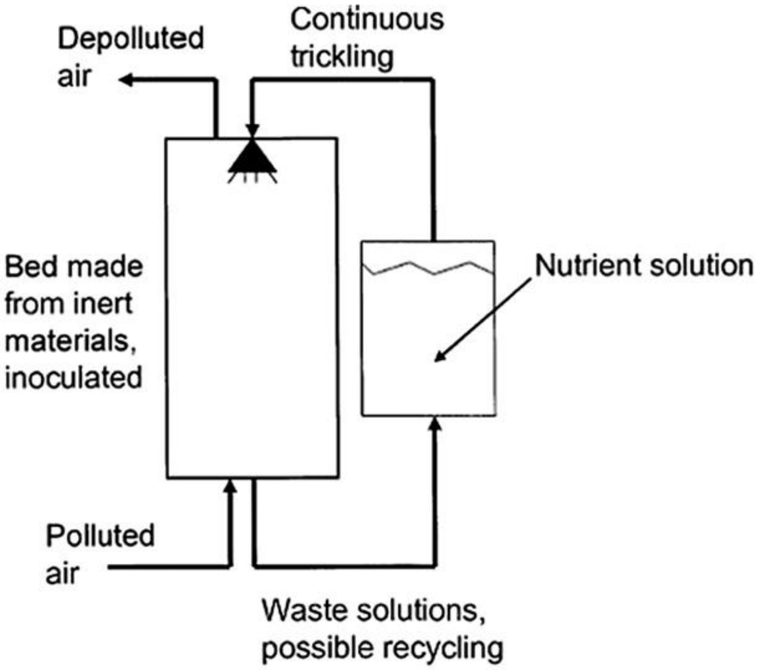


Figure 3-5: Schematic of biotrickling filter (adapted from Mudliar et al., 2010)

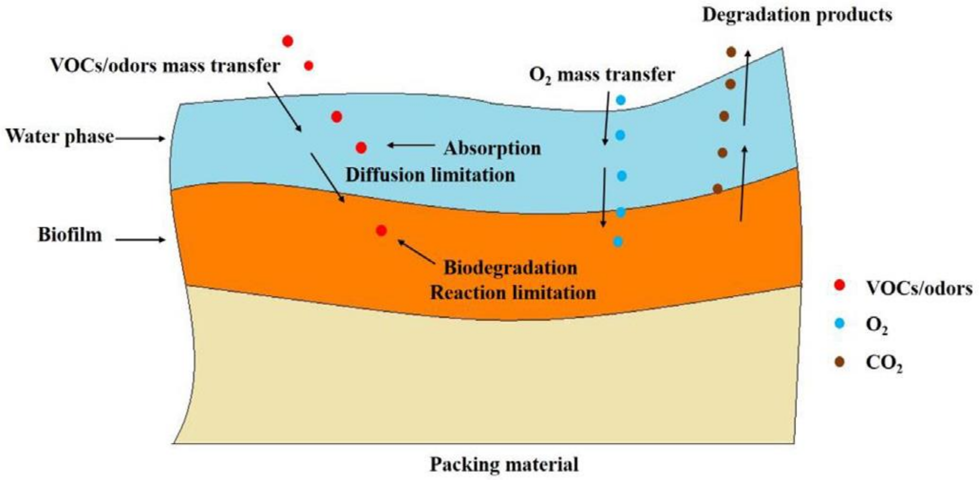


Figure 3-6: Phenomena involved in the operation of biotrickling filter (adapted from Wu et al., 2018)

In the biofilm, where actually the biodegradation process is carried out, may occur the formation of secondary metabolites, which can be subjected to diffusion, biodegradation and adsorption processes in the same way of primary pollutants.

In fact, it is possible to transform these metabolites to the end products (such as CO2). However, when secondary metabolites are characterized by higher toxicity then original pollutants their formation can cause the inhibition of biodegradation process.

For example, Purswani et al. (2011) and Skiba et al. (2002) have found that the production of p-benzoquinone during the biodegradation of chlorophenolor 4-chloronitrobenzene and accumulation of tert-butyl alcohol during the transformation of methyl tert-butyl ether (MTBE) are related to the stopping of biological reactions.

In the case of the removal of hydrocarbon vapors, the primary degraders are aerobic heterotrophic.

The biofilm immobilized on the supports contained in the reactor bed and continuously humidified and irrigated by a circulating nutrients enriched water medium, to ensure the absorption of pollutants and nutrients by the microorganisms and to eliminate the exceeding biomass and secondary metabolites. Consequently, the contaminated air do not require pre-humidification due to the presence of trickling liquid (Estrada et al., 2011; Muñoz et al., 2015; Schiavon et al., 2016).

Compared to the conventional biofilter, BTFs exhibit clear advantages in terms of process stability, pH control, lower pressure drops and volume needed. These conditions are ensured by the continuous trickling of water and nutrients (Lebrero et al., 2014; Mudliar et al., 2010).

On the counter part, the water layer over the biofilm may entail a reduced elimination capacity for hydrophobic compounds. The addition of silicone oil in the trickling solution resulted in both an enhanced abatement performance and in a higher process robustness (Lebrero et al., 2013).

The reactor bed is supported by the wall, which should be able to ensure structural support to the bed, resistance to corrosion and thermal insulation. In that view, the real-scale reactors are made of glass fiber, polypropylene, polyethylene or polyvinyl chloride (PVC). The circulating liquid media is homogenously distributed on the top surface of the bed by nozzles and may be passes through a heat exchanger to keep the liquid temperature constant. The pH control can be obtained by adding sodium hydroxide.

Co-current and countercurrent flow-configurations are both possible. The BTFs, differently from BFs, require inoculation with microorganisms from an external source because the packing material is inert (Bajpai, 2014). The packing media should be characterized by a large specific area, high porosity, high chemical stability and structural strength, low weight, suitable surface for bacterial attachment and growth and low cost (Barbusinski et al., 2017).

Balasubramanian et al. (2012) evaluated the performance of a biotrickling filter (BTF) treating complex mixtures of VOCs from pharmaceutical industries. In particular, the model pollutants considered were methanol, ethanol, acetone and toluene. Inlet load ranged between 52 to 419 g $m^{-3}h^{-1}$, while the EBRT from 25 to 69 s. When treating mixed pollutants, the BTF was able to completely degrade the VOCs up to an IL equal to 240 g $m^{-3}h^{-1}$. For single pollutants, RE equal to 100% was achieved for IL up to 320 g $m^{-3}h^{-1}$.

Hu et al. (2016) investigated the performance of a BTF for pharmaceutical VOCs removal. The system was inoculated with specified strains of Zoogloea resiniphila HJ1 and Methylobacterium rhodesianum H13, to improve the removal of recalcitrant VOCs due to slow microbial adaptation and growth.

The model mixture was composed of pharmaceutical VOCs containing toluene, o-xylene and dichloromethane in a specific BTF was investigated.

During the operation, the BTF supported efficiency of 96–100% for a net inlet concentration between 450 and 600 g m^{-3} at an empty bed retention time (EBRT) of 30–75 s. The maximum elimination capacity (EC) recorded was equal to 114.3 g $m^{-3}h^{-1}$ for an IL of 135 g $m^{-3}h^{-1}$.

The main advantages of BTFs are the low operating and capital costs, lower pressure drop during long-term operation and capability to intensively treat acidic degradation products of VOCs. At the same time BTFs are relatively complex in construction and operation and accumulate excess biomass (Lebrero et al., 2012; Mudliar et al., 2010).

BTFs allow a better control of pH, nutrient supply and moisture along with an higher removal of toxic metabolites (Seignez et al., 2004).

In addition, BTFs support an enhanced biodegradation due to the enrichment of pollutants with extracellular polymeric substances which work as surfactants (Balasubramanian et al., 2012).

Among the main drawback of this technology, the mass transfer from gas to liquid phase may results in limitation. Similarly to what occur in BFs, the increase of biofilm thickness can reduce the empty volume of the carrier and thus increase the pressure drop (Kennes and Thalasso, 1998).

3.1.3 Bioscrubbing

The bioscrubber is a two-stage reactor consisting in an absorption column, where the pollutants get absorbed into an aqueous solution, and an interconnected suspended growth bioreactor, where the biological oxidation of the pollutant into the aqueous media takes place (Figure 3-7)

The gaseous and liquid phases flow countercurrently within the column. In the column packing material may be added to increase transfer surface between the VOCs and liquid.

The addition of emulsifying agents (silicon oil, phthalate) in the aqueous solution could enhance the elimination of scarcely soluble compounds, thanks to the higher affinity with VOCs, increasing the mass transfer from gas to the liquid phase as well (Mudliar et al., 2010).

The bioscrubbing promotes the elimination of polluting compounds from waste gas with the following concomitant mechanisms (Singh et al., 2010):

- the absorption process promote the transfer of pollutants from the gas into the aqueous phase. The effectiveness of the mass transfer depends on the contact surface area, EBRT and diffusivity coefficient;
- the adsorption process is based on the attraction of the higher molecular weight compounds (with low water solubility) which may be physically adsorbed to biological flocs;
- the condensation mechanisms allow to transfer the gaseous compounds at higher temperature into the aqueous medium maintained at a lower temperature;
- the biodegradation or biotransformation reactions are promoted by active microorganisms. The contaminants transferred into the liquid phase are

degraded by these microorganisms, which use VOCs as source of organic carbon to provide both energy and carbon for cell growth and synthesis.

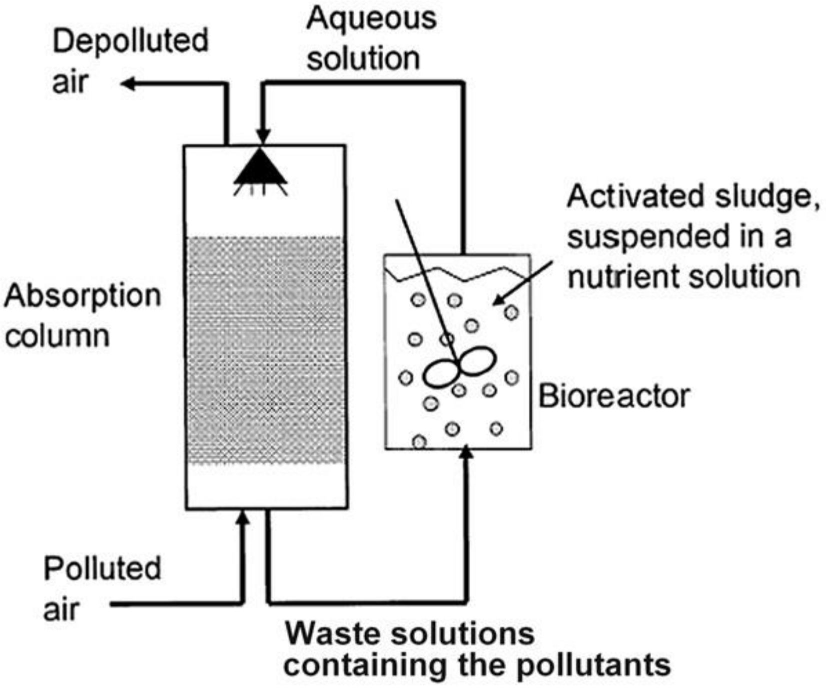


Figure 3-7: Schematic of bioscrubbing (adapted from Mudliar et al., 2010)

Bioscrubbing represents a possible solution for the treatment of high pollutant concentrations and large gas flows, since in these conditions biotrickling filters shows a limited suitability.

The main advantages of BS are operational stability and effective control of operating parameters such as pH and nutrients dosage, relatively low gas pressure drop and small space requirement (Mudliar et al., 2010).

In addition, concentrations of toxic byproducts generated in the reactor can be maintained at low levels thanks to the higher buffer capacity (Singh et al., 2010).

Disadvantages include possible excess sludge generation, washing out of microorganisms, limited application for less water-soluble compounds (Wu et al., 2018).

3.2 Chemical-physical treatments

The existing of numerous industrial applications of well established and emerging physical -chemical processes, both for recovery and destruction of VOCs, boosted the interest in these treatments technologies. The chemical-physical technologies which emerged as the most implemented solutions includes adsorption, thermal oxidation, catalytic oxidation, absorption, condensation, membrane separation (Malakar et al., 2017).

3.2.1 Adsorption

Adsorption is a heterogeneous reaction in which gaseous compounds may be retained on a solid or liquid surface, which work as adsorbent.

The adsorbent material present specific affinities with certain compounds that, consequently, may be removed from the contaminated streams (Yükseler et al., 2016).

The adsorption technology is one of the most effective recovery method for the treatment of waste gases contaminated by low concentrations, since the relatively moderate operating costs.

The AC is recognized as the most used adsorbent as a result of its high specific surface and the extended adaptability for a wide variety of applications (Aguayo-Villarreal et al., 2017).

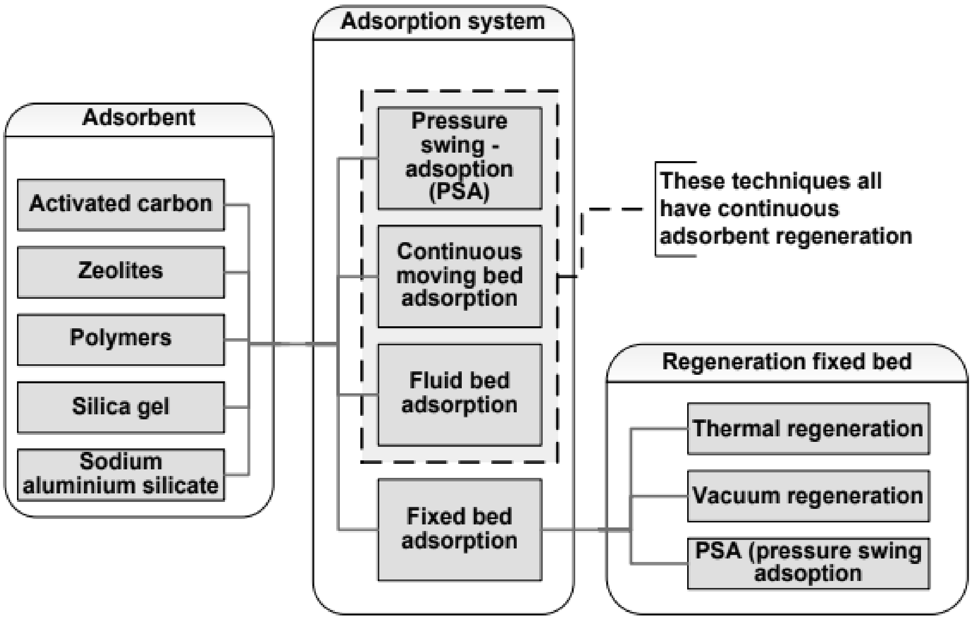


Figure 3-8: Overview of different adsorption systems, adsorbents and regeneration processes used (adapted from BAT, Yükseler et al., 2016)

The major types of adsorption systems are reported in Figure 3-8:

- fixed-bed adsorption in which the gas is fed at about 40 °C to upwards the adsorber. The most used configuration envisages multiple-bed (two or more);
- fluid-bed adsorption is based on the capacity of gas (velocity range between 0.8 and 1.2 m/s) to maintain fluidized the adsorbent material. A continuous adsorption/desorption operation mode is envisaged; the adsorbent material is regenerated into in a heat exchanger and returned pneumatically to the fluidised bed;
- continuous moving-bed adsorption, in which the adsorbent is continuously add from the top of the reactor, countercurrently to the gas stream. a moving-bed regenerator is isnstalled downstream for the continuously regeneration of the saturated adsorbent;
- pressure swing adsorption (PSA) promotes the separation of gases or vapours in a waste gas mixture according to the strength with which they bond to the adsorbent and the simultaneous regeneration of the adsorbent with downstream facilities.

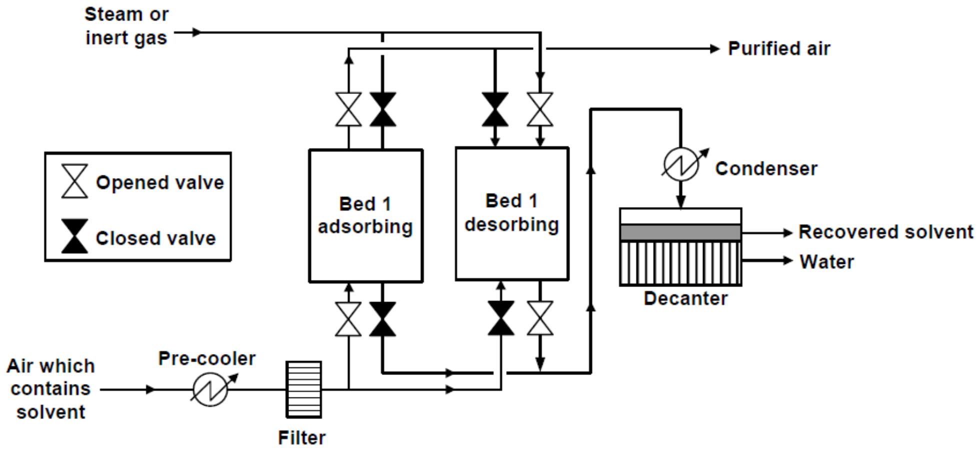


Figure 3-9: Schematic of a twin bed adsorption process (adapted from BAT, Yükseler et al., 2016)

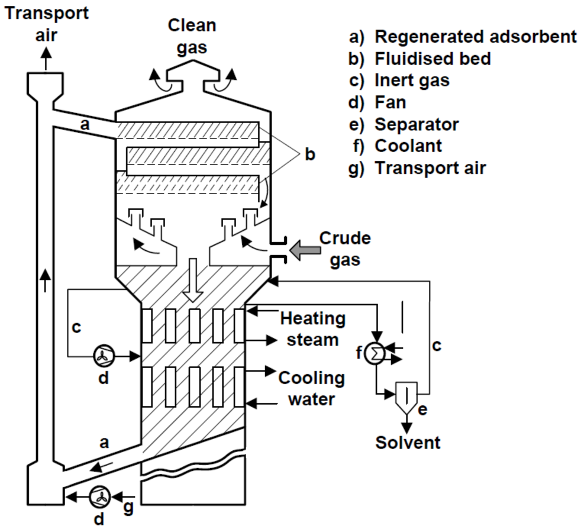


Figure 3-10: Schematic of a fluidised-bed adsorption (adapted from BAT, Yükseler et al., 2016)

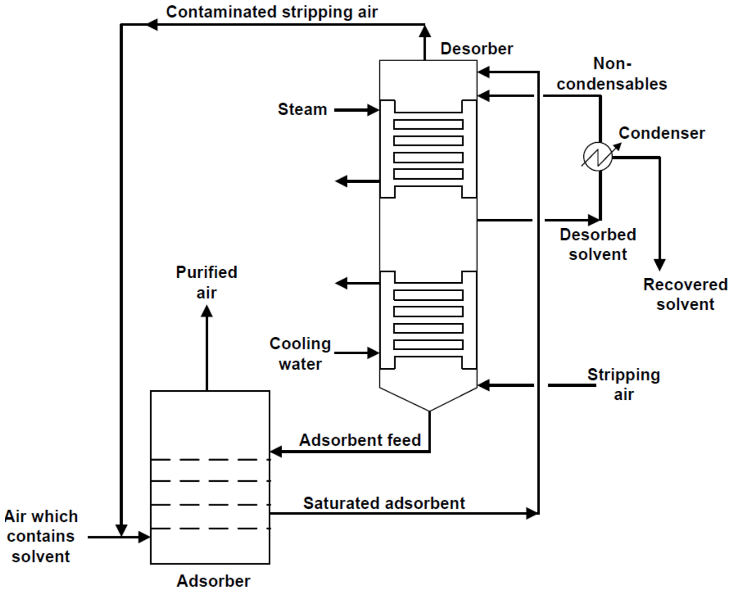


Figure 3-11: Schematic of continuous moving-bed adsorption and desorption (adapted from BAT, Yükseler et al., 2016)

The typical adsorbents are listed below (Yükseler et al., 2016):

- activated carbon (AC);
- zeolites;
- macroporous polymer particles;
- silica gel;
- sodium-aluminum silicates.

The identification of the most adequate porous solid adsorbent is the key aspect for the application of the adsorption technique. Carbon based materials are widely recognized to exhibit some advantages as low-cost, high-efficiency and good-stability VOC abatement, in spite of some inherent disadvantages such as hygroscopicity and pore blocking. For the identification of the adsorbent materials it should be taken into consideration that a large specific surface area and small pore size may enhance the adsorption.

The acidic functional groups are good at adsorbing polar VOCs, whereas the basic groups has a higher affinity with non-polar VOCs. Furthermore, a larger size of VOCs molecular cross-sectional area may inhibit the diffusion into the adsorbents pores. Compounds with high boiling point are easier to adsorb and, consequently, to desorb for recovery purpose as well.

Temperature and gas phase water vapor content may affect process performances; in fact, low temperature is conductive since entails over-whelming physical exothermic interaction, while water vapor presence negatively influences the adsorption capacity because water molecules may occupy the pore available for VOCs adsorption (Zhang et al., 2017).

Zeolites are characterized by thermal stability, resistance to humidity, possibility to regenerate and highly ordered porous structure (Beauchetet al., 2007; Canet et al., 2007). Furthermore, the zeolites work both as adsorbent and catalyst, exhibiting a clear advantage over the rest of activated carbon (Baek et al., 2004) (Swetha et al., 2017).

3.2.2 Condensation

Condensation is a process able to remove solvent vapors from a waste gas stream. The mechanism is based on the reduction of the temperature below the dew point. The condensation processes are classified in:

- coolant condensation (temperature down to about 25 °C);
- refrigerant condensation (temperature down to about 2 °C);
- brine condensation (temperature down to about -10 °C);
- ammonia brine condensation (temperature down to about -40 °C for one-stage or -60 °C for two-stage);
- cryogenic condensation (temperature down to about -120 °C;
- closed-cycle inert gas condensation.

Condensation is carried out by means of direct contact between gas and cooling liquid or indirect cooling by means of a heat exchanger (*Figure 3-12*). The second configuration is preferred since does not require an additional separation stage (Yükseler et al., 2016).

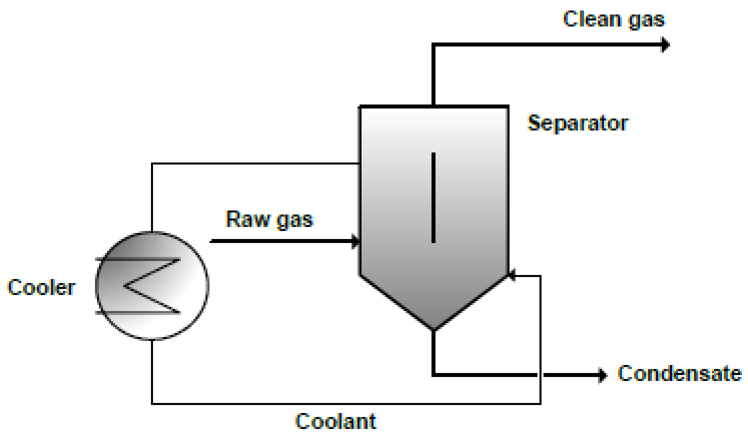


Figure 3-12: Schematic of a condenser system (adapted from BAT, Yükseler et al., 2016)

The direct condensation application rises an attractive interest since it is envisaged the possibility to recovery VOCs directly as liquid with a physical, non-destructive, separation process. However, this method involves cryogenic operation when the target condenser temperature is lower than 30° C. This necessity occurs for low contaminants incoming loads or low boiling points (Belaissaoui et al., 2016).

3.2.3 Thermal oxidation

Thermal oxidation, also called incineration, thermal incineration or oxidative combustion, is an oxidation process which promote the heating of the gaseous contaminants in a combustion chamber, with temperature above the auto-ignition point of the target compounds (Yükseler et al., 2016). The temperature are maintained high for the complete conversion of the VOCs to carbon dioxide and water. The range of temperature of these oxidation systems for VOCs combustion is between 1,300–1,800°F.

Temperatures near 1,800°F may be related to the high production of nitrogen oxides and, thus, require further treatment. Thermal energy recovery systems allow to recover the heat of the outlet stream to warm up the inlet stream before the combustion.

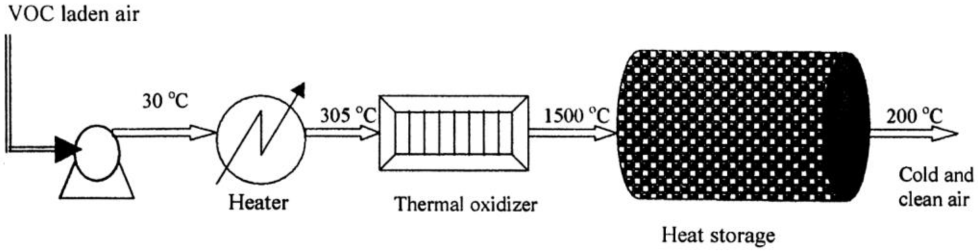


Figure 3-13: Schematic of a regenerative thermal oxidation system (adapted from BAT, Khan and Kr. Ghoshal, 2000)

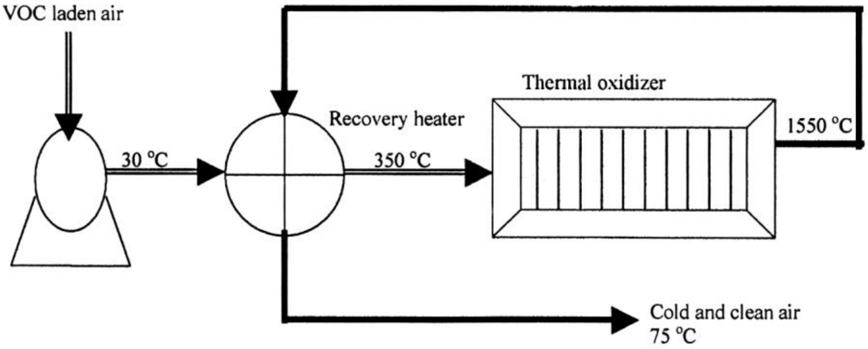


Figure 3-14: Schematic of a recuperative thermal oxidation system (adapted from BAT, Khan and Kr. Ghoshal, 2000)

In the recuperative system, ceramic beds are used to capture heat from the gas outgoing the combustion zone. Recovery of the thermal energy input to the system as fuel and the heat content of the combusted VOCs up to 95% have been recorded using multiple beds.

In the recuperative thermal oxidation systems, the heat is typically recaptured by means of a simple shell-and-tube metallic heat exchanger, with maximum thermal energy recovery around 70% of the fuel and VOC combustion energy input to the system.

The advantage recuperative systems over the regenerative system are related to the shorter time required to reach effective operating conditions, due to the larger mass of the regenerative heat recovery system (Khan and Kr. Ghoshal, 2000).

3.2.4 *Catalytic oxidation*

In catalytic oxidation systems, the waste gas passes through a flame area and then in a catalyst bed (Figure 3-15). The catalyst bed aims at increasing the oxidation rate, promoting conversion reactions at lower temperatures and with lower volumes than those required in thermal oxidation systems (Yükseler et al., 2016).
The temperatures at which VOCs are oxidized ranges between 523 and 723 K; these relatively low temperatures involve lower additional energy consumption and minimized NOx formation (Yuxi Liu et al., 2016).
Based on the methods with which the gas stream is in contact with the catalyst, it is possible to classify the systems in (Yükseler et al., 2016):

- fixed-bed catalytic oxidizer, which consists of monolith catalyst or a packed-bed catalyst. The monolith catalyst is a porous solid block in which parallel channel are aligned with gas flowrate direction;
- packed-bed catalyst, which consists of tube or in shallow trays, covered by catalysts particles, in which the gas flows.

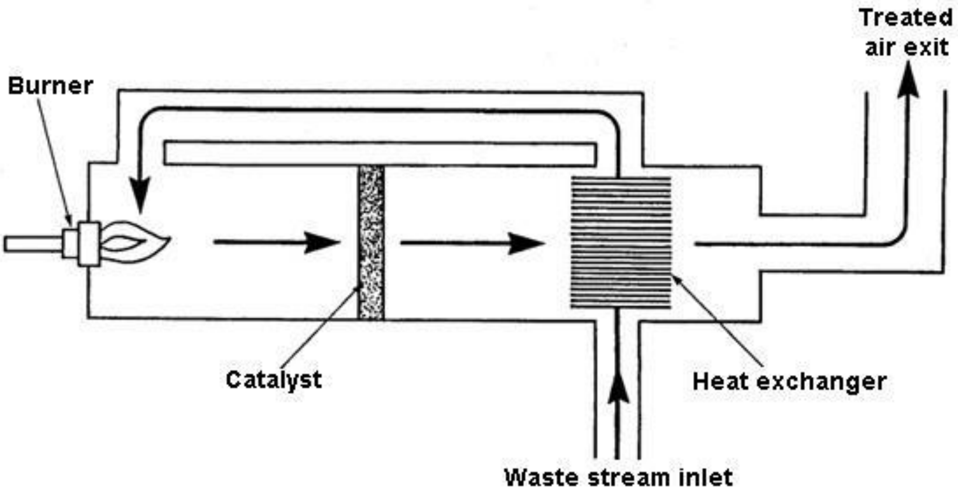


Figure 3-15: Schematic of a catalytic oxidation system (adapted from BAT, Yükseler et al., 2016)

The research in this application aims at realizing effective and low cost materials able to catalyse the complete oxidation of VOCs into CO_2 and H_2O.
The most promising catalysts are classified into two different classes (L. Liu et al., 2017):

- supported noble metals catalysts, in spite of their more expensive costs, are preferred because of their high specific activities at low temperatures;

- transition metal oxides (TMOs) catalysts, including combustion metal oxide catalysts, pure transition metal oxides, mixed transition metal oxides, and perovskites represent efficient low cost alternatives for VOCs combustion.

The materials used as catalysts for VOC oxidation purposes are precious metals, including platinum, palladium and rhodium, whose supports are typically ceramic or metal carriers, base metals supported on ceramic pellets, metal oxides supported by a strong carrier, like oxides of copper, chromium, manganese, nickel, cobalt. Highly active oxidation for benzene, toluene, butanol and 1-hexene were obtained with platinum and palladium over alumina (Ribeiro et al., 2019).

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4. Advanced Oxidation Processes as emerging technologies for the abatement of gas pollutants

Advanced oxidation processes (AOPs) are technologies mutated from the treatment of water and wastewater. These processes rely on the production of strong oxidants with high oxidation potential.

The high performances recorded for the removal of contaminants in the aqueous phase increased the interests in the application of these technologies for different matrix.

In particular, the application of AOPs for the removal of gaseous compounds have been found to be an effective solution for the treatment of VOCs and odours.

The main application of AOPs as single stage processes and in combination with other technologies, along with their weaknesses and strengths are overviewed in this chapter.

4.1 Single stage AOPs Treatment Technologies

4.1.1 Non-Thermal Plasma

Plasma is defined as an ionized gas characterized by not-balanced charges, the so-called fourth state of ions and electrons. Plasmas are classified as equilibrium and non-equilibrium plasmas (Son et al., 2015).

N_2, O_2 are the most used bulk gas molecules, bombarded by the electrons which promotes the production of excited gas molecules (N_2*, O_2*). Subsequently, these molecules lose their excess energy by emitting photons or heat (Karatum and Deshusses, 2016).

In the discharge zone, along with excitation, other processes like ionization, dissociation and electron attachment occur take place. Free radicals are thus produces, including OH• and O•, highly reactive species employed for the conversion of pollutants into CO_2, H_2O and other degradation products at low temperatures (Schmidt et al., 2014).

Non-equilibrium plasmas envisage multiple temperatures because of the different energies of the particles (charged and neutral) and the different degrees of freedom (Fridman et al., 2005; Ragazzi et al., 2014)

The electrons exhibit temperature ranging between 104 and 105 K, exceeding those of heavy particles. Consequently, radicals and excited neutral species can take place, with a concomitant low translational temperatures (300–400 K). This is the reason why non-equilibrium plasmas are known as Non-Thermal Plasma (NTP). Conversely, in equilibrium plasmas the particles have the same temperatures, exceeding 104 K; they are thus called “thermal plasma” (Fridman et al., 2007; Marotta et al., 2008).

The mechanism is based on the condition that electrons and their surrounding are not in thermal equilibrium. Consequently high energy electrons, active radicals and ions are produced and result in chemical reactions in the ionized zones. In particular, ozone (O_3), oxygen atoms [$O(^1D)$ and $O(^3P)$], hydroxyl radicals, and free electrons, with destructive effect on gaseous pollutants are generated (Karatum and Deshusses, 2016; Mista and Kacprzyk, 2008).

Non-thermal plasma (NTP) is an emerging air pollution technology with the potential to treat high flowrates from both low to high (>1000 ppmv) concentrations of pollutants (Karatum and Deshusses, 2016; Penetrante and Schultheis, 1993).

In NTP, the energy is mainly used for energetic electrons production, without heating the gas flowrate.

Different type of discharges, including spark, corona, gliding arc or dielectric barrier discharges (DBD) have been investigated (Hoffmann, 2013; Holladay et al., 2009; Indarto et al., 2006; Liang et al., 2011; Matsumoto et al., 2012)

In particular, DBD plasma, also called silent discharge, obtained a great attention thanks to the possibility to reach high decomposition efficiency especially for low concentration of VOCs in a cost-effective way (Abdel-Salam et al., 2003; Kundu et al., 2012; Mustafa et al., 2018; Valdivia-Barrientos et al., 2006).

In dielectric barrier discharge, micro-discharges are formed when the local electron density in the discharge gap reaches a critical value. The micro-discharges are bright, thin filaments distributed by a dielectric in the discharge volume, initiating chemical reactions, with a low selectivity to total oxidation and a consequent by-products production (Subrahmanyam, 2009).

DBD plasma reactor, moreover, provide a simpler experimental setup and stable and reproducible plasma conditions (Jian Hu et al., 2016; Mei and Tu, 2017; Ragazzi et al., 2014).

DBD, as shown in Figure 4-1, has at least one glass, quartz or ceramic dielectric between the electrodes.

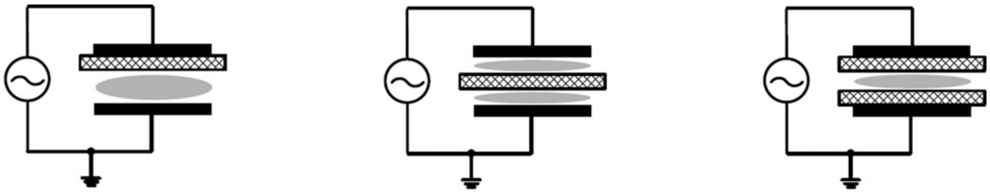
The dielectric in the discharge zone has two main function: limiting the charge transferred by an individual micro-discharge and spreading the micro-discharge over the electrode surface with a concomitant increase in the probability of electron–

molecule collisions with bulk gas molecules (Yamamoto et al., 1992). This arrangement is known as volume discharge (Pietsch, 2001).

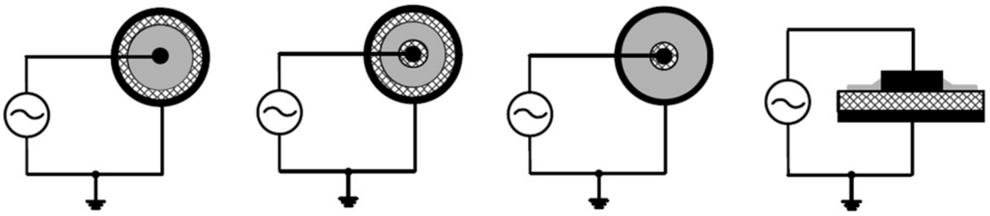
Also in the surface discharge different configurations are possible. In Figure 4-1c, for example series of strip electrodes are attached to the surface of a high-purity alumina ceramic base. Planar or cylindrical ceramic base works as induction electrode (Vandenbroucke et al., 2011).

In Figure 4-1d, a pulsed corona discharge is reported. In this configuration, a pulsed power supply with a fast voltage rise time (tens of nanoseconds) is applied to enable an increase in corona voltage. The voltage required to energize the discharge is a function of the distance between the electrodes, the pulse duration and the gas composition (McAdams, 2001).

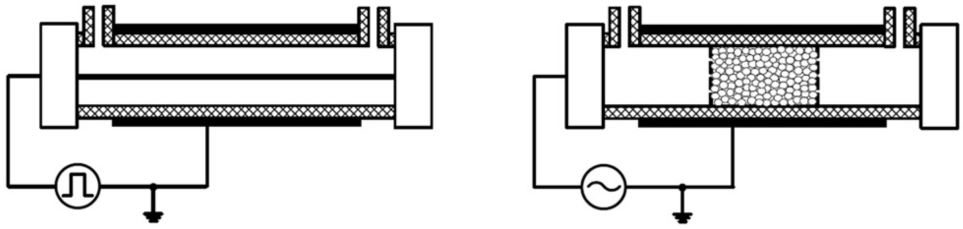
A ferroelectric pellet packed-bed reactor is reported in Figure 4-1e. It consists of a packed-bed reactor filled with perovskite oxide pellets. Either parallel-plate or a coaxial configuration are possible. An external electric field is applied to polarize the ferroelectric material and induce strong local electric fields at the contact points.



(a) planar DBD configurations



(b) cylindrical DBD configurations (c) surface discharge



(d) pulsed corona discharge (e) ferroelectric pellet packed-bed reactor

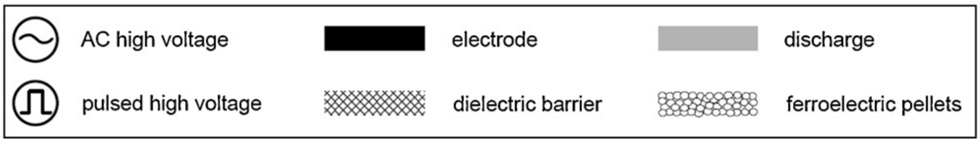


Figure 4-1: Schematic of various NTP reactor configurations (adapted from Vandenbroucke et al., 2011).

In general, in NTP, to energize electrons electrical energy is used (1–10 eV) for ionisation and excitation of gas molecules instead of gas heating. This aspect triggers the application of NTP due to the energy-savings potential respect to thermal oxidation (Mista and Kacprzyk, 2008).

However, also NTP requires significant quantity of electrical energy (Kim, 2004; Oda et al., 1993; Parmar and Rao, 2008; Yamamoto et al., 1992).

In particular, more than >70 J L-1 are needed to efficiently decompose VOCs and odorous compounds (Lu et al., 2006; Marotta et al., 2008; Oda et al., 1993; Ruan et al., 2005; Ch. Subrahmanyam et al., 2010; Xia et al., 2008).

These technologies exhibits also scale-up problems because of their relatively low average energy (20 eV) and energy deflection near the electrodes, which may resulting in incomplete decomposition of the pollutants (Parmar and Rao, 2008).
The process sustainability of NTP reaction should be further improved by reducing power consumption and the undesired byproducts formation.

4.1.2 Electron-Beam

Electron beam irradiation is included among NTP formation method. In Figure 4-2, it is reported the schematic representation of electron beam source. In this technique, the electrons are accelerated by high voltage in the vacuum region and then injected into a chamber thorough a thin foil window (Matsumoto et al., 2012).
Differently by NTP electrical discharge methods (e.g. DBD), in which the gas is directly injected into plasma to generate energetic electron and radicals, electron beam produces non-thermal plasma by supplying energetic electrons to the gas.
The energy is thus used for the dissociation and ionization of gaseous molecules. In particular, during the ionization process, a shower of ionized electrons is created (Chmielewski et al., 2004; Duarte et al., 2002; Matsumoto et al., 2012).

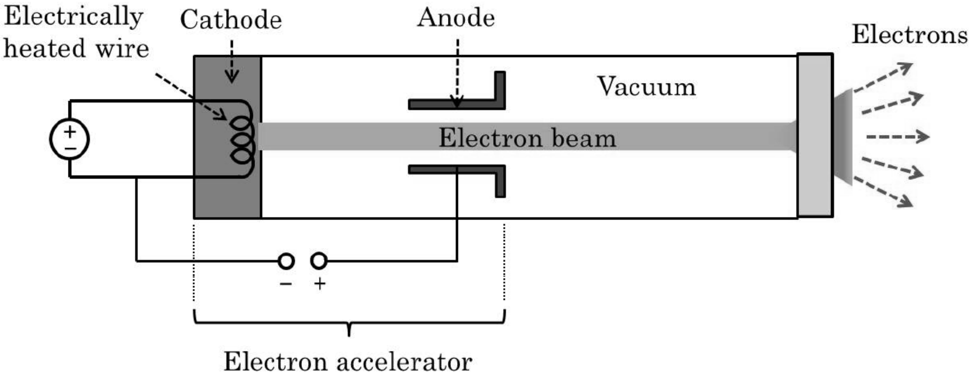


Figure 4-2: Schematic of electron beam source (adapted from Matsumoto et al., 2012).

The electron beam is created by means of an EB accelerator; different accelerator configurations have been proposed for wastegas treatment purposes: transformer accelerator, ultrahigh frequency (UHF) accelerator and linear microwave accelerator (Chmielewski et al., 2004; Son, 2017).
The process generates electrons every 10^{-18}–10^{-12} s (Kim, 2002; Kim et al., 2012). The efficacy depends on the reaction with active species, which are oxidizing radicals such as OH and HO_2 and excited ions as $O(^3P)$ (Hirota et al., 2004).

These species act in ion-molecule reactions, neutralization reactions, and dimerization (A. G. Chmielewski, 2007).

In EB process, energy is absorbed by bulky gaseous molecules proportionally to their mass fraction in the mixture, expressed as absorbed dose (kGy) according to the following equation.

$$Absorbed\ dose\ [kGy] = \frac{Energy\ adsorbed\ dose\ per\ second}{Product\ mass\ per\ second}$$

Which means that 1 kGy provides energy of 1.19 J L-1to gases at ambient air temperature (Hirota et al., 2004).

The primary electrons produced by the EB irradiation are then provided to ionize the air by exciting the N2, O2 and H2O in the background gases. In that way, radicals, ions and secondary electron are produced (A. G. Chmielewski, 2007; Chmielewski et al., 2007; Licki et al., 2003; Son et al., 2010b, 2013).

Different studies have been conducted with a view at comparing plasma, photocatalyst, electron beam (EB) and their hybrid systems (Calinescu et al., 2008; Hakoda et al., 2009, 2010; Kim et al., 2012; L. Liu et al., 2017; Son et al., 2015, n.d.).

In particular, some authors investigated the decomposition of some VOCs including toluene, benzene and styrene variating the initial concentration of contaminants and the absorbed dose. As expected, it was found that RE of VOCs by EB irradiation improved as their initial concentrations decreased and the absorbed doses increased (Han et al., 2003; Hashimoto et al., 2000; Kim, 2002; Kim et al., 2005; Sun et al., 2013)

Son et al. (2010a) studied the REs of toluene increasing the inlet concentration from 100 to 400 ppm and the corresponding removal yields decreased from 67% to 53% respectively.

Sun et al. (2013) recorded that at an absorbed dose of 58 kGy, the RE of toluene decreased from 94% at 32 ppm to 19% at 481 ppm. Moreover, Son (2017) evaluated the performance of EB for the removal of styrene at 200 ppm, which resulted in RE of about 63% at 2.5 kGy and approximately 91% at 10 kGy.

The studies also suggested that the RE curve of VOCs resulted non-linear, probably due to back reactions or presence of low reactivity toward OH radicals.

The opportunity of use technologies for environmental protection have gained a great interest, but for the application at industrial scale some advancements are need to overcome the main problems of undesired by-products formation and window foils corrosion.

In particular, some recent studies have focused the attention on the use of non-corrosive material for the primary and secondary window foils production, to increase the sustainability of the process for long-term operation (Andrzej G. Chmielewski, 2007; Son, 2017; Technical Meeting on Deployment of Clean (Green) Radiation Technology for Environmental Remediation and International Atomic Energy Agency, 2016)

4.1.3 *Photocatalytic oxidation*

Photocatalytic oxidation, also called photocatalysis, is a technology for the degradation by oxidation of different compounds including VOCs, sulphur compounds, nitrogen compounds, odours, and bacteria.

Two-step reactions are involved in the process requiring a catalyst and an irradiation system to activate the catalyst; both ultraviolet (UV) rays from artificial lamps or sunlight are used (Yükseler et al., 2016).

The electronic band structure of photocatalytic materials is reported in Figure 4-3. A band gap (E_g) separates the valence band (V_B) filled with electrons and a vacant conduction band (C_B). This gap represents an energy barrier for the electrons.

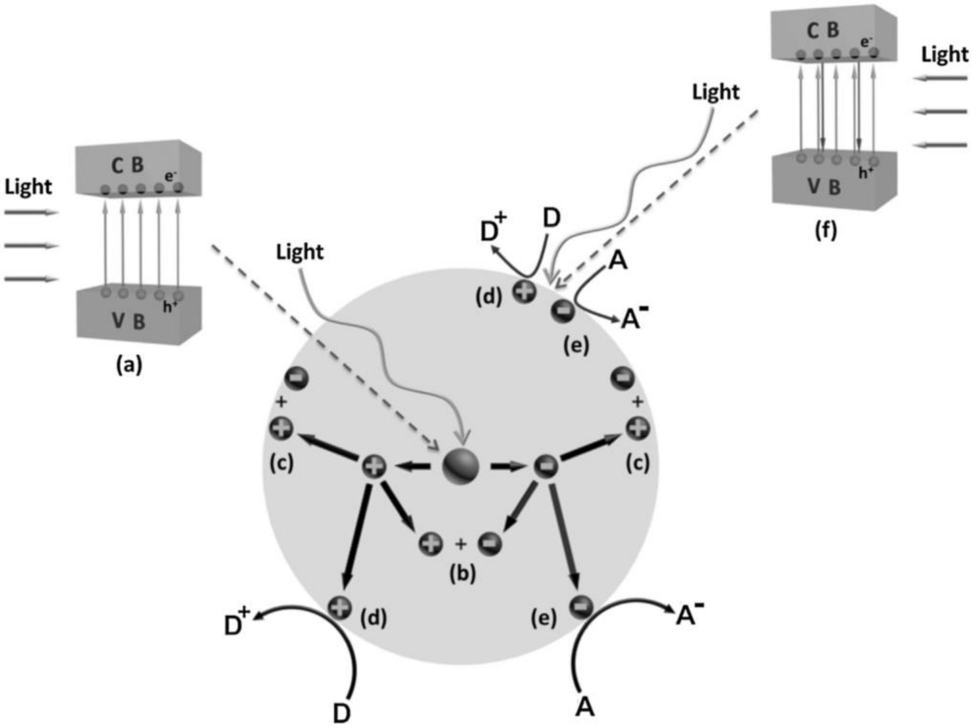


Figure 4-3: Schematic diagram of photocatalysis: (a) electronic excitation by light of a molecule in bulk of photocatalyst (b) electron and holes recombination in bulk, (c) electron and hole recombination at grain surface, (d) hole reaction with electron donor (D) adsorbed on grain surface, (e) electron reaction with electron acceptor (A) adsorbed on grain surface, (f) electronic excitation by light of molecule at grain surface of photocatalyst and localized recombination. (adapted from Ren et al., 2017)

The radiation provides the energy of photon to the semiconductor and if this energy is enough it allows to the electrons in the valence band to bridge to the conduction band. The holes in the valence band became available to diffuse to the surface of the photocatalyst. The active sites promotes the adsorption of environmental species and the redox reactions can take place (Linsebigler et al., 1995; Schiavello, 2013).
This general mechanism is studied with the following equation:

$$A + e^{-} \rightarrow \bullet\, A^{-} \qquad 1)$$

$$D + h^{+} \rightarrow \bullet\, D^{+} \qquad 2)$$

Where • is unpaired electron, A is electron acceptors which can react with electrons (e^{-}) by reduction and holes (h^{+}) can react with electron donors (D) by oxidation.

The combined action of UV and catalyst convert water vapour into two highly reactive, strong oxidisers: hydroxyl radicals (OH) and superoxide ions (O^{2-}) (Liu et al., 2011; Mills and Le Hunte, 1997; Ren et al., 2017; Schiavello, 2013).

In particular, TiO_2 activated under ultraviolet UV irradiation (400–315 nm) generates electrons and positively charged holes on its surface. The positively charged holes on TiO_2 have a high oxidation potential of 2.53 V. Moreover, the positively charged holes react with molecular water adsorbed on the surface of photocatalyst to produce hydroxyl radicals according to the following equation (Debono et al., 2017; Huang et al., 2013; Paz, 2010).

$$TiO_2 + hv \rightarrow h_{VB}^{+} + e_{CB}^{-}$$

$$e_{CB}^{-} + O_2 \rightarrow O_2^{\cdot -}$$

$$h_{VB}^{+} + H_2O \rightarrow OH^{\cdot} + H^{+}$$

h_{VB}^{+} is the positively charged hole in a valence band, the $OH^{\bullet}$ radical has an even higher oxidation potential (2.80 V) than the positively charged hole and react quickly with a wide range of compounds via a relatively non-selective process (Bahnemann, 2004; Fujishima et al., 2000; Hashimoto et al., 2005).

The photocatalytic oxidation is a process which operates at relatively low temperature and pressure. Consequently, the removal of organic compounds may be economically feasible using economical photocatalysts.

The materials utilized as photocatalysts include TiO_2, WO_3, $SrTiO_3$, Fe_2O_3, SnO_2, ZnO, ZnS and CdS (Hussain et al., 2017).

TiO_2 is an ideal photocatalyst with strong oxidation power and good resistance to corrosion. Moreover, it is non-toxic and able to operate at lower temperature under more economical and energy-savings conditions (Bhatkhande et al., 2002).

The process effectiveness is influenced by the particle size and specific area of TiO_2 (Su et al., 2004).

Photocatalytic reactor systems can be classified, according to their configuration, in plate, annular, honeycomb monolith, and fluidized-bed reactors (Ren et al., 2017).

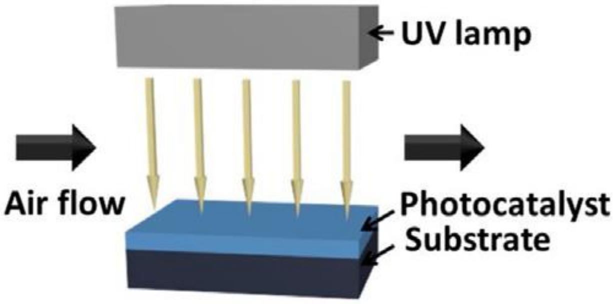


Figure 4-4: Schematic diagram of plate reactor configuration (Adapted from Ren et al., 2017)

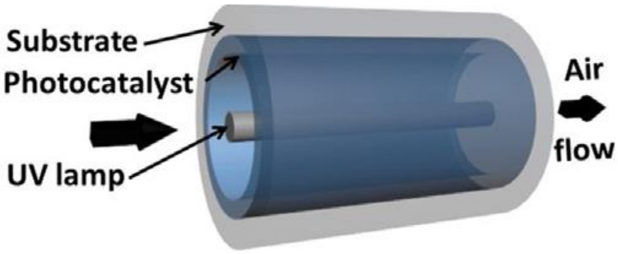


Figure 4-5: Schematic diagram of anular reactor configuration (Adapted from Ren et al., 2017)

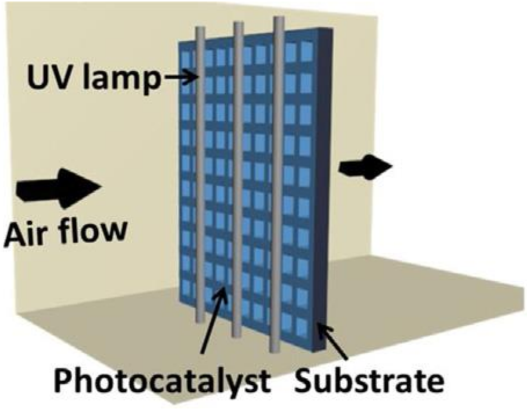


Figure 4-6: Schematic diagram of honeycomb monolith reactor configuration (Adapted from Ren et al., 2017)

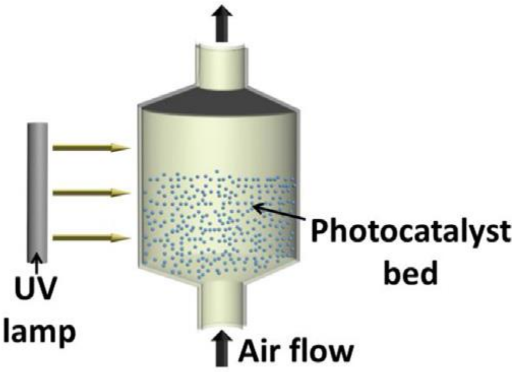


Figure 4-7: Schematic diagram of fluidized-bed reactor configuration (Adapted from Ren et al., 2017)

The combination of UV-LED and a honeycomb structure may ensure larger reaction area, higher mass transfer rate and higher reaction rate.

The pathways for VOCs photocatalytic degradation are still under investigation, with a particular interest in the generation of harmful intermediates (i.e. carcinogenic substances). It has been demonstrated that the concentrations of oxygen and hydroxyl radicals play a significant role in the reaction pathways and the formation of different intermediates.

Consequently, the control of the reactions could be realized by the adjustments of oxygen and water vapour concentrations (Ren et al., 2017).

However, the key parameter which influence the removal efficiency and by-products generation include VOC concentration, relative humidity, light intensity and residence time.

Mamaghani et al. (2018) founded that by increasing the Relative Humidity (RH) from 0 to 20%, the performances of the process resulted higher since the formation of more hydroxyl radicals via reaction between adsorbed water with holes.

Further increase in RH, at 50%, caused a reduction in removal yields related to the adsorption competition between VOC and water molecules for active sites on catalyst and also because of the presence of water film on its surface which inhibits the contact between pollutants and catalyst.

The same authors investigated the influence of residence time on the removal efficiency; in particular, it was found that increasing the time obviously the efficiency is enhanced due to the extended time for the adsorption and reaction of the pollutants.

The removal efficiency exhibited inverse proportion to VOCs inlet concertation, since the reduction in the ration between “active sites + reactive species” to VOC molecules. In the study, it was also observed that the light intensity influenced the number of photons generated and consequently the number of pairs of electrons and holes.

The photocatalytic process is considered a good option for the effective removal of gaseous VOCs. However, some process limitations should be overcame, including relatively low oxidation rate, formation of toxic by-products and catalyst deactivation.

To this end, the optimisation of the process parameters, synthesis of highly active catalytic materials and implementation of accelerated and efficient catalyst regeneration may help for a more efficient treatment balance (Krichevskaya et al., 2017).

A great attention in the scientific literature is given to the enhancement of the photocatalytic activity of TiO_2 with a view at extending the range of photo efficiency into visible light by doping the semiconductor with various types of metal (Fe, Mn, Au and Ag) and non-metal atoms (N, F, S and Br) (Joung et al., 2006; Khalilzadeh and Fatemi, 2014; Wu and Chen, 2004).

The doping could decrease the band gap energy of TiO_2 and improve the interfacial charge transfer and trapping of electrons, thereby reducing the recombination rate of the photo-generated electrons and holes (Khan and Berk, 2014; Pham and Lee, 2017).

4.1.4 Ozone oxidation

Ozone oxidation is also a potential technique that is widely applied for the degradation of VOCs (Kwong et al., 2008; Lu et al., 2012; Yuan et al., 2013).

Gas-phase ozone is a strong oxidizing agent and capable of reacting with numerous gas and aqueous-phase organics, including VOCs (Boeniger, 1995; Kwong et al., 2008). Thus, ozonation as single stage process and in combination with other treatment technologies has been extensively investigated as destructive methods for the removal of natural or anthropogenic VOCs emissions in air and water (Bouchaala, 2012).

Although it has been demonstrated the efficacy of the treatment for volatile organic compounds (VOCs), the experimental remained at lab-scale (Cheng et al., 2015; Waring and Wells, 2015) and no computational effort were observed in the literature (Mohan et al., 2017)

Ozone molecules could combine with VOC molecules at their double bonds. The products are unstable and could be further degraded to reactive radicals which could undergo subsequent decomposition reactions of VOCs. However, the removal efficiency of VOCs solely exerted by ozone oxidation is somewhat low (Chen et al., n.d.). Consequently, the combination of ozone oxidation with other techniques, including adsorption and photocatalysis might be another option to enhance the decomposition of VOCs (Kwong et al., 2008; Yu and Lee, 2007; Zhang and Liu, 2004; Lu et al., 2012; Yuan et al., 2013).

4.2 Hybrid Technologies

The combination of individual AOPs techniques with other technologies are found to be more cost-effective and attractive solution compared to the single-stage treatment.

Treatment systems using only AOPs exhibited many demerits including low RE for high concentration of VOCs and formation of undesirable by-products (Son, 2017; Zhang et al., 2016).

Moreover, it has been assessed that VOCs removal by AOPs may be characterized by three main weaknesses: (i) incomplete oxidation with emission of harmful compounds (CO, NOx, other VOCs), (ii) poor energy efficiency and (iii) low mineralization degree (Vandenbroucke et al., 2011).

The combination with conventional waste gas treatment technologiescould thus emphasize the effectiveness of AOPs, reducing the negative impacts.

The combined use of adsorption followed by ozone oxidation has been investigated and exhibited a potential for its implementation at industrial scale. Ozone can destroy adsorbed molecules with a concomitant regeneration of the zeolite adsorption capacity (Brodu et al., 2013; Monneyron et al., 2003; Zaitan et al., 2016).

The adsorption of VOCs on several kinds of zeolites followed by ozonation ensured a high degree of recovery on the adsorption capacity of zeolites, due to the fact that with this hybrid technologies molecular ozone generates very powerful free radicals after ozone adsorption and its decomposition on strong Lewis acid sites of zeolite surface, leading to the oxidation of adsorbed VOCs (Alejandro et al., 2014; Brodu et al., 2013).

The combination of NTP with photo-catalysis was evaluated to overcome one of the major drawback of NTP technology, related to by-product formation, including CO formation. The attention has been paid to generate more oxygen active species to further oxidize CO into CO_2.

In that view, heterogeneous catalyst has been extensively combined with NTP.

Two different configuration are possible (Van Durme et al., 2008):

- introducing the catalyst in the discharge zone (Figure 4-8) (in plasma catalysis, IPC);
- placing the catalyst after the discharge zone (Figure 4-9) (post plasma catalysis, PPC).

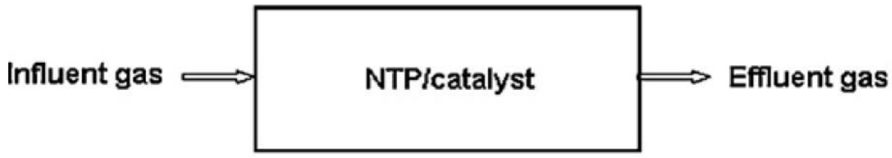


Figure 4-8: Schematic of in-plasma configuration (IPC) (adapted from Van Durme et al., 2008)

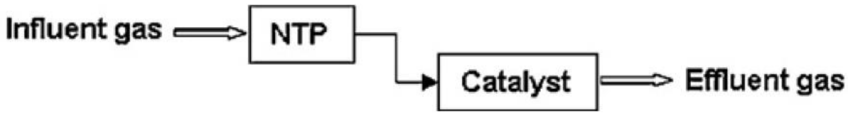


Figure 4-9: Schematic of post plasma configuration (PPC) (adapted from Van Durme et al., 2008)

In the heterogeneous catalysis, the material can be introduced into the reactor as coating on the reactor wall or electrodes, as a packed-bed, including granulates, coated fibres, pellets or as a layer of catalyst material, including powder, pellet, granulates, coated fibre (Figure 4-10).

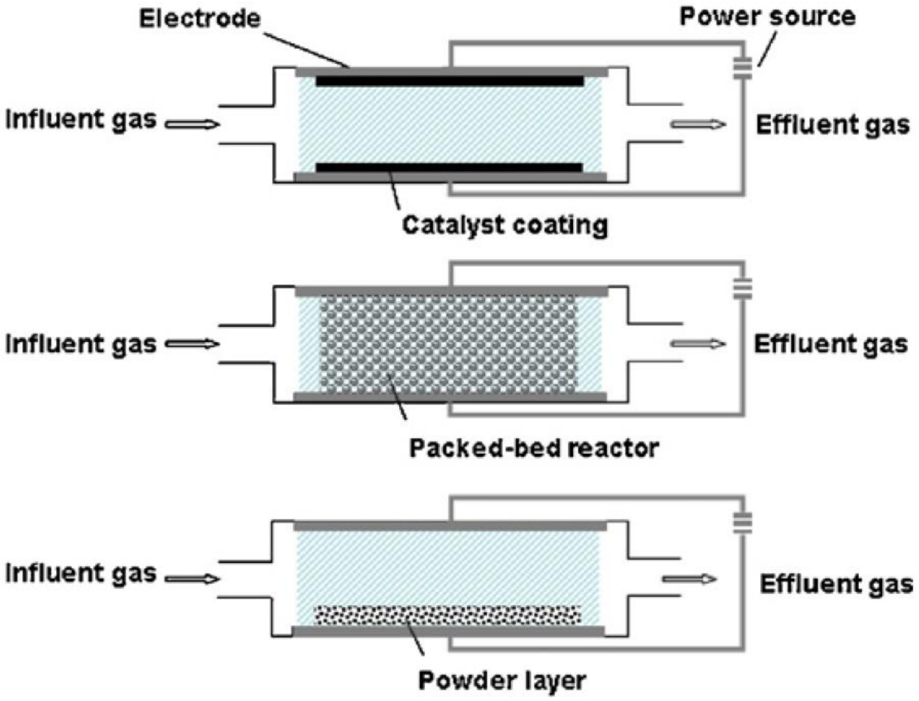


Figure 4-10: Schematic of catalyst insertion methods for IPC configuration (adapted from Van Durme et al., 2008)

Vacuum UV-photolysis also attracted an interest for VOCs removal, by using UV light emitted from lamps at a wavelength of 185 nm. The photons generated can react with oxygen and water vapor to produce reactive species such as $O(^1D)$, $O(^3P)$, hydroxyl radicals (•OH) and O_3.

Even if this process have been applied for the destruction of benzene, toluene and methyl-benzene, it exhibited some drawbacks as the low degradation capacity and mineralization rate for VOCs destruction and large quantities of residual ozone.

Since ozone is a well-known strong oxidant it can be also decomposed to enhance VOC. Despite the fact that direct oxidation of VOCs by ozone alone can hardly destroyed the contaminants below the desired levels, it has been investigated its combination for the assistance of catalysts. In that view, it would be considered the combination of VUV photolysis with ozone-assisted catalytic oxidation (OZCO). The main mechanisms involve the VOCs destruction by the VUV photolysis and then be further oxidized by the OZCO using the residual ozone from the VUV photolysis; the ozone was removed and used for the simultaneous further enhanced degradation of VOC (Huang et al., 2016a).

As previously reported, biofiltration has been worldwide recognized as the most simple and cost-effective alternative for low-concentration VOCs gas treatment. However, biofilters often may be clogged by excess biomass for long-term operation. The main existing strategies for biomass control in biofilters are stirring and backwashing. The addition of chemicals negatively affects the economical sustainability of the process and the microorganisms and their biodegradation. Ozone has been identified as a potential option for biomass control. Thus the combination of biofiltration with ozone supply is a promising method to enhance process stability and biomass control (Saingam et al., 2018).

Ozonation supported by ultraviolet irradiation (UV/O_3) is a promising method to degrade recalcitrant and hydrophobic VOCs (Z. W. Cheng et al., 2013). Ozone enhances the degradation capability of the combined process not only due to its high oxidation potential, but also by the formation of strong oxidants such as hydroxyl and oxide radicals (Z. W. Cheng et al., 2013).

Ozone was produced by the irradiation of air with the UV lamps, based on the reactions reported below (Jeong et al., 2005).

$$\mathrm{O_2 + hv \rightarrow O(^1D) + O(^3P)}$$
$$\mathrm{O(^1D) + M \rightarrow O(^3P) + M}$$
$$\mathrm{O(^3P) + O_2 + M \rightarrow O_3 + M}$$

The photolysis/irradiation of ozone than leads to the hydroxyl radicals formation (Jeong et al., 2005).

$$\mathrm{O_3 + hv \rightarrow O(^1D) + O_2}$$
$$\mathrm{O(^1D) + H_2O \rightarrow 2OH\cdot}$$

The presence of water vapor irradiated with UV also generate additional radicals by the mechanism of the reaction shown by Eqn. 6 (Johnson et al., 2014a). However, the further irradiation of ozone lead to the greater contribution of hydroxyl radicals.

$$\mathrm{H_2O + hv \rightarrow H + OH\cdot}$$

Different studies evaluated the performances of toluene oxidation by UV/O_3, varying different operational parameters, including inlet concentration, ozone concentration, gas flow rate and humidity, using UV lamps and separate ozone generators (Pengyi et al., 2003a; K. P. Yu and Lee, 2007).

These studies suggested that the UV/O3 process is a suitable technology with the aim at degrading toluene. The main disadvantage of the application of UV/O3 treatment is the formation of undesirable by-products resulting from the UV irradiation and ozone oxidation (Zhan et al., 2018a).

5. Photosynthesis-based technology for CO_2 fixation

Green energy production along with global warming is one of the topics which rises much interest in the sectors of industry, technology and life science (Sydney et al., 2010).

The treatment of industrial waste gas may involve intensive energy requirements and high carbon foot-print. Thus, the definition of appropriate solution to mitigate these drawbacks and to implement sustainable strategies for the recovery of energy and materials from waste gas is of key interest.

The global warming concerns are mainly related to anthropological discharge of CO_2 emissions, which is the main component of greenhouse gas emissions (GHGs).

Nowadays, the reduction in atmospheric CO_2 concentration is among the most important issues facing the world. In particular, the usage of fossil fuels are one of the major sources of anthropological emission of carbon dioxide.

Consequently are under investigation the optimization and the research of alternative strategies to utilize carbon dioxide or minimize its emissions to ensure environmental sustainability.

A sustainable pursued strategy for GHGs reduction with a simultaneous energy production involves the generation of energy from reduced-carbon-emission sources. Biofuel is considered a good alternative to the fossil fuels, with the real chance that it can play a significant role in the reduction of transportation related CO_2 emissions.

In recent years, the biofuels use and its production has increasingly risen as a result of global energy crisis and the concomitant rise in awareness about the importance of sustainability and the environment aspects (Uduman et al., 2010; Zeng et al., 2011).

The conventional available technologies for CO_2 removal/capture are physical-chemical absorbents, injection into deep oceans and geological formations, and enhanced biological fixation. The latter is considered the primary economically feasible and environmentally sustainable technology in the long term (Sydney et al., 2010).

In particular, biological CO_2 mitigation via microalgae has attracted much more attention since it combines both environmental and economic interests.

Algae have been indeed identified as one of the preferred feedstocks to produce fuels due to their fast growth rate, carbon-neutrality and sustainability (Pegallapati et al., 2012; Wijffels and Barbosa, 2010).

Carbon dioxide is converted into biomass by autotrophs, with nutrient utilization and energy feedstock production.

In that view, the use of microalgae for biofuel production has gained such interest related to their capability to photosynthetically convert CO_2 into potential biofuel biomass, as well as food, feed stocks and high value biochemical (Kumar et al., 2010).

5.1 Microalgae cultivation

The fixation of carbon dioxide promoted by microalgae can be implemented from different sources, including CO_2 from the atmosphere as well as from industrial exhaust gases.

CO_2 can be used as source of carbon for the photosynthetic activity and for the recovery of enhanced oil and natural gas recovery, among others. The usage of photosynthetic microorganism as sink for carbon dioxide is an attractive method for CO_2 sequestration (Zeiler et al., n.d.).

Thanks to the capacity of microalgae to grow faster than the terrestrial plants, the efficiency to fix CO_2 can range from 10 to 50% (Ho et al., 2011).

The sequestration of carbon dioxide in aquatic environment by microalgae is related to the Henry′s Law and, thus, temperature of the liquid and partial pressure of CO_2 are the driving factors.

The microalgae exhibits the capacity to accumulate CO_2 up to 12% at 35°C while most plants can accumulate carbon dioxide up to 0.1%. Flue gases from power plants and industrial exhaust gases contains up to 13% of carbon dioxide and, thus, it could be of particular interest their use as carbon sources (Demirbas, 2011; Mata et al., 2010; Tang et al., 2011; Valdés et al., 2012).

In particular, the utilization of waste gas has gained a significant importance since it provide a potential carbon source for the cultivation of microalgae and the possibility to simultaneously bio-fix CO2 and abate contaminants concentrations. Furthermore, it allows to overcome the main drawback for the industrial cultivation of microalgae related to the cost of the media for the cultivation (Sydney et al., 2010).

Microalgae exhibit different advantages over the other plant feedstock, including (Wang et al., 2008; Zeng et al., 2011):

- high photosynthetic conversion efficiencies;
- rapid biomass production rates;

- the capacity to produce a wide variety of biofuel feedstock;
- ability to thrive in diverse ecosystems;
- distinguished environmental bioremediation;
- not-competitiveness for land with crops and non-competitiveness with the food market.

As shown in Figure 5-1, CO_2 fixation by microalgae cultivation allow to produce biomass easily and directly convertible to biofuels for energy production following different process steps (Zeng et al., 2011):

- cultivation;
- harvesting;
- dewatering;
- extraction;
- transesterification.

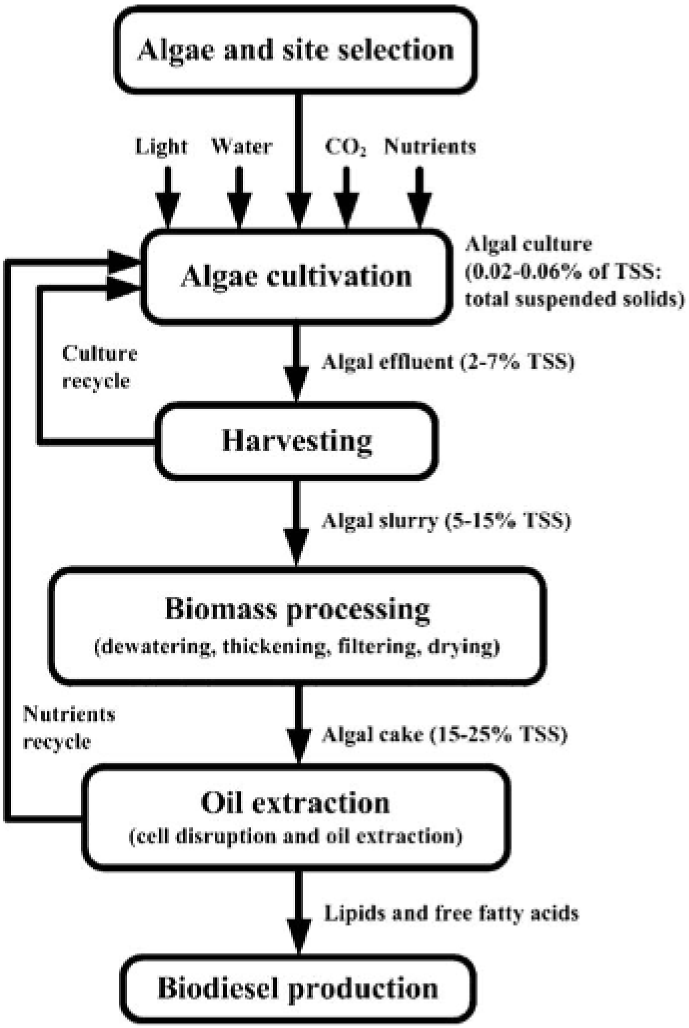


Figure 5-1: Microalgae biodiesel value chain stages (Adapted from Mata et al., 2010)

The microalgae metabolism is based on photosynthetic upper-pathway. The rate of carbon uptake is limited by the metabolic activity of microalgae, which is in turn limited by photosynthesis. Gaseous contaminants can be utilized as carbon sources for producing bio-oil, biodiesel, food additives, pigments, and cosmetics with a concomitant CO_2 capture in intensive cultures.

Microalgae cultivation may be implemented in closed system and open ponds as well; however, the cost of closed systems resulted significantly higher than open ponds, requiring approximately ten times the capital investments of raceway ponds.

Since microalgae cultures are typically carried out in closed photo-bioreactors for the optimal control of the operating conditions (Olivieri et al., 2015), the reduction of the cost related to closed system is mandatory to promote the success of biofuel production via microalgae cultivation (Brennan and Owende, 2010; Demirbas and Fatih Demirbas, 2011; Singh et al., 2014).

5.2 Photobioreactors

Photo-bioreactors (PBRs) are widely used in cultivation of microalgae since the possibility to better ensure optimal light, temperature, nitrogen starvation, and input of nutrients, resulting in a high biomass productivity and lipid yields (Singh et al., 2014).

PBRs can be classified according to the overview reported in the

Figure ***5-2***.

The main parameters considered for the classification are (Kroumov et al., 2016; Pegallapati et al., 2012):

- the penetration and distribution of the light, depending on fluid flow distribution;
- the surface-to-volume ratio, which influences microalgal kinetics and PBR performance;
- energy input and types of aeration, which influence hydrodynamics and mass transfer.

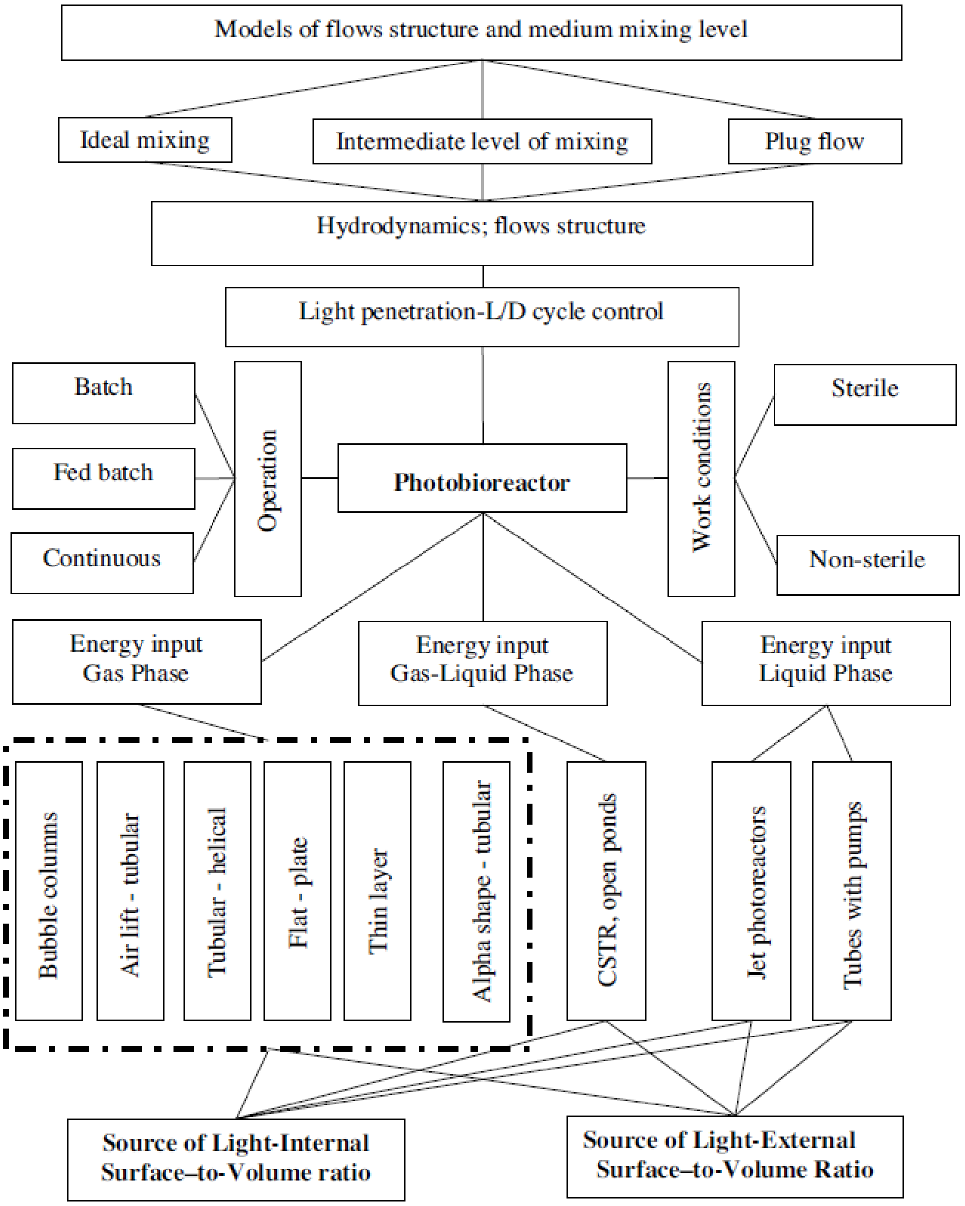


Figure 5-2: Photobioreactors configuration (Adapted from Kroumov et al., 2016)

The design of photo-bioreactors should pursuit not only the maximization of biomass productivity but also the net energy gain, in order to make the process an energy efficient and sustainable solution. To maximize the net energy gain, the first strategy is to minimize the energy input, which includes the light energy input for illuminating the cultures and the energy input for providing the gas and mixing the cultures and keeping them suspended (Pegallapati et al., 2012).

A second strategy is to maximize the lipid content of the algal biomass by implementing different possible approaches. These approaches include stressing the cultures by nitrogen depletion (Chiu et al., 2009; Li et al., 2008), phosphate limitation (Reitan et al., 1994), high salinity (Rao et al., 2007), high iron concentration (Liu et al., 2008) or light control.

A key parameter for the evaluation of algal PBRs for biofuel could be the biomass productivity per unit energy input (B/E). The B/E ratio recorded in different studies ranges between 0.03 to 1.42 $gW^{-1}d^{-1}$ (Ge et al., 2011; Hsieh and Wu, 2009; Hulatt and Thomas, 2011; Liu et al., 2008; Reyna-Velarde et al., 2010; Ryu et al., 2009).

The energy required for the dispersion of the gas is approximately 10–100 times lower than the energy needed for the light in the artificially lit PBRs. However, this parameter became critical in the case of outdoor PBRs for large-scale cultivation (Sierra et al., 2008).

The energy expended for sparging per unit culture volume depends on the reactor height and the G/V ratio, where G is the gas flowrate and V the volume of the reactor. In Figure 5-3 it has been reported the effect of G/V ratio on biomass production (B), sparging energy (Es), biomass production per unit sparging energy input (B/Es) and biomass production per unit energy input (B/E) studied by Pegallapati et al. (2012). It can be observed that when the G/V ratio increases, biomass productivity increases as well up to a certain point, remaining constant thereafter.

Conversely, as expected, the sparging energy continued to increase directly with G/V ratio.

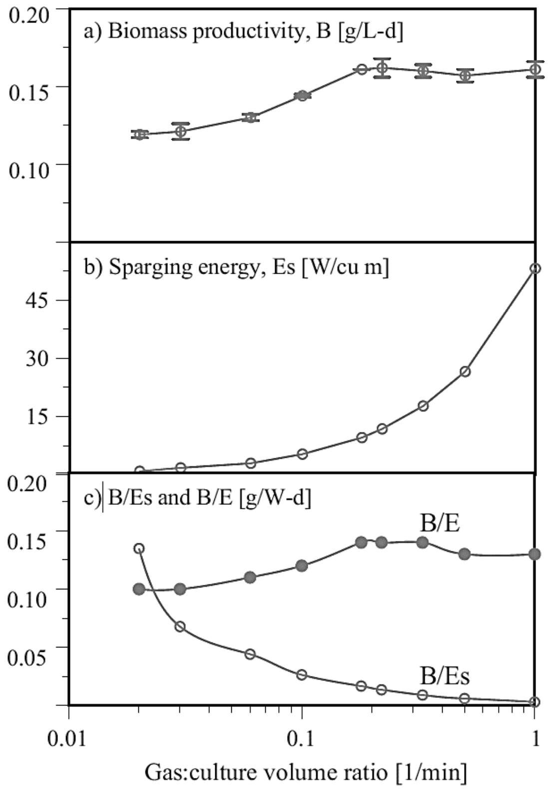


Figure 5-3: Effect of gas-to-culture volume (G/V) ratio on: (a) Biomass production (B); (b) sparging energy (Es); (c) biomass production per unit sparging energy input (B/Es) and biomass production per unit energy input (B/E) (Adapted from Pegallapati et al., 2012).

Energy required for the artificial illumination is the dominant energy claimed from artificially lit PBRs, and, consequently, has a strong influence on productivity and energy efficiency (Pegallapati et al., 2012).

To reduce the light energy consumption, the use of light emitting diodes (LEDs) can be considered a good solution for increasing cost effectiveness than the use of fluorescent light (Singh et al., 2014).

On the basis of literature data, comparing different configuration of PBRs toward light energy input per unit culture volume (Ei/V ratio), the configuration with the lowest light input are the flat panel airlift photobioreactor (FPA-PBR) (Ei/V = 127.1 Wm^{-3}), the internal illuminated photobioreactor (IIPBR) (Ei/V= 276.4 Wm^{-3}) and the transparent rectangular chamber photobioreactor (TRC-PBR) (Ei/V = 399.1 Wm-3) (Ge et al., 2011; Hsieh and Wu, 2009; Hulatt and Thomas, 2011; Liu et al., 2008; Pegallapati et al., 2012; Reyna-Velarde et al., 2010; Ryu et al., 2009).

Furthermore, as shown in Figure 5-4, B/E is seen to decrease with increasing incident area per unit culture volume, since the the incident area increase with the light input and biomass productivity does not continue to increase in proportionally (Pegallapati et al., 2012).

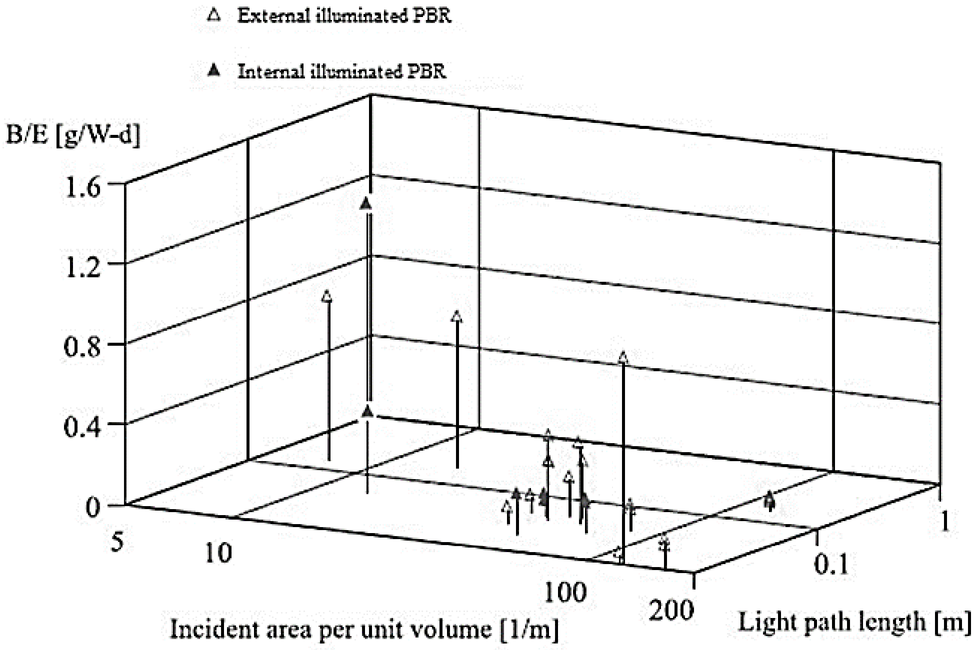


Figure 5-4: Effect of B/E estimated for PBRs using literature results as a function of incident area per unit volume and light path length.

Nowadays, the complete replacement of fossil fuels by biofuels it seems still economically unfeasible. However, biofuels exhibit the potential to support the transition from current petroleum based society towards a green biofuel based society, thanks to the extended researches in this direction (Singh et al., 2014).

Moreover, the benefits deriving from combining wastewater purification and waste gas treatment may significantly increase the attraction of these technologies as cost-effective and competitive solutions (Kroumov et al., 2016); combining savings for the wastegas and wastewater treatment and reducing the costs of microalgae production is a win–win strategy while producing energy or biofuels (Lam and Lee, 2012; Zamalloa et al., 2011).

In the waste gas biological treatments sector, the synergisms between microalgae and bacteria in photo-bioreactors represent an efficient platform for an enhanced contaminants mineralization and a concomitant photosynthetic fixation of the resulting carbon dioxide.

Despite their advantages, the number of studies exploring the merits of algal-bacterial photobioreactors for waste gas treatment resulted still scarce (Lebrero et al., 2016a).

6. Research Experimental Activity

Different kind of treatment technologies have been developed to eliminate VOCs below harmless level, such as incineration, catalytic combustion and photocatalytic oxidation, which demonstrated to support high performance for VOCs degradation (Huang et al., 2016b; Xie et al., 2019).

However, the possibility to overcome the major drawbacks of the current treatment technologies is consistent with legislative directives in the field and with the need to minimize costs, energy and environmental pressures.

The research for innovative solutions in this field has thus gained a great relevance, with the objective to optimize cost-effective and environmental friendly treatments, required to adequately remove VOCs and odours from industrial waste gas stream.

Chemical-physical treatments are among the most used technologies and consequently they are characterized by an established knowhow. They do not support the degradation of the gaseous compounds, but only the transfer of the contaminants from the gas to the solid or liquid phase (Boyjoo et al., 2017).

On the contrary, biological and oxidation processes are able to promote the partial or complete degradation of these organic compounds, resulting into their mineralization. Consequently, these processes do not require further treatment of the phases to which the contamination may be transferred (Oliva et al., 2018; Angèles et al., 2018).

In particular, AOPs are based on the action of active species with high redox potential, such as hydroxyl radicals (HO°, 2.8 eV), which could oxidize organic compounds into harmless compounds, including H_2O, CO_2 and other mineral salts (Andreozzi, 1999; Oturan and Aaron, 2014). These processes has been mutated from the application at water and wastewater treatment and disinfection.

Although the high performance which are possible to achieve with AOPs treatments applied for VOCs abatement, the release of toxic by-products and the high energy demand are the main factors which limited their application at industrial scale.

In that view, the wet scrubber coupled with a specific advanced oxidation process represents a promising way for to overcome these limitation, promoting a cost-effective and environmental sustainable VOCs degradation (Chen et al., 2018; Zhan et al., 2018b).

In fact, it has been demonstrated that their combination in hybrid system allows to conveniently enhance liquid-gas mass transfer and promote the following degradation in aqueous phase (Biard et al., 2009).

The degradation promoted by these hybrid processes mainly includes four steps (Tokumura et al., 2008, 2012b):

- mass transfer of the waste gas from gaseous phase to aqueous phase;
- generation of active species from AOPs;
- degradation of dissolved VOCs;
- treated gas separation from aqueous phase.

In particular, in ozonation supported by ultraviolet irradiation process (UV/O_3), the ozone was produced by the irradiation of air with the UV lamps (Jeong et al., 2005). It is considered a promising method for the degradation of recalcitrant and hydrophobic VOCs, thanks to the enhanced degradation capability promoted by ozonation not only due to ozone oxidation potential, but also by the formation of hydroxyl and oxide radicals (Z. W. Cheng et al., 2013).

The high solubility of the ozone by-products in water may rise the synergism between the above-mentioned process and absorption process.

On the other hand, the application of physical-chemical processes for the abatement of toluene-laden waste gas streams could be inconvenient when treating high flow rates with relatively low VOCs concentrations.

Alternatively, at reduced IL, biological processes have demonstrated high removal efficiencies for the aerobic biodegradation of toluene at lower operating costs and reduced environmental pressures (Lebrero et al., 2010).

Among biotechnologies, biotrickling filters exhibit clear advantages over their biological competitors, exhibiting a better process stability and pH control and, consequently, a reduced sensitivity to the acid-producing pollutants presence, along with lower pressure drops and lower footprints thanks to the continuous trickling of water and nutrients (Lebrero et al., 2012; Mudliar et al., 2010; Angèles et al., 2018).

However, since the occurrence of oxygen limitation is often detected in these systems because of the low water-solubility of VOCs, different strategies have been worldwide implemented to enhance biological process stability.

In this context, the synergic effects between microalgae and bacteria has been proposed as an efficient platform to support the simultaneous abatement of CO_2 and VOCs, with the oxidation of organic compounds by heterotrophic bacteria which utilize the additional O_2 produced by the photosynthetic activity of microalgae in the presence of light (Lebrero et al., 2016a).

Furthermore, the fixation of carbon dioxide results in biomass build-up which can be further valorized into added-value products (Toledo-Cervantes et al., 2017).

Based on these evidences, in this work were proposed:

- a novel solution for the efficient elimination of gaseous VOCs by wet scrubber coupled with UV/O_3 process, for the treatment of relatively high concentrated waste gas streams;
- an innovative algal-based tubular photo-bioreactors for the simultaneous abatement of carbon dioxide and VOCs, with a concomitant algal biomass production.

6.1 Experimental plan

The overall aim of this research is the identification of novel solutions for the removal of gaseous volatile organic pollutants by the application of a hybrid advanced technology and an enhanced biotechnologies, to balance removal performance, cost-effectiveness and environmental protection purposes.

To this end, experimental activity was structured in two main steps:

- the comparative assessment of the single-stage UV/ozonation process and the system coupled with wet scrubbing, to address the treatment of concentrated emissions;
- the comparative evaluation of a conventional biotreatment technology (BioTrickling Filtration, BTF), and an innovative photobioreactor (TPBR) for the enhancement of biological degradation.

Toluene was selected as the model VOC due to the facts that it is among the most common VOCs found in the industrial emissions, is toxic for human health and is listed among the hazardous air pollutant by EPA (Ghanbari and Moradi, 2017).

The research first step pursued the following objectives:

- the definition of the optimal operating conditions for both the investigated processes (UV/O_3 and UV/O_3+S);
- the investigation of the roles of absorption and oxidation process in toluene elimination with the hybrid system;
- the evaluation of the applicability of the proposed system for the waste gas treatment.

In order to state the optimal operating conditions, the UV lamps voltage and, consequently, the ozone dose, was variated.

The influence of ozone dosage and toluene inlet concentrations was evaluated to assess removal yields and the gaseous by-products release.

Since the high solubility of gaseous by-products and their oxidation potential in water phase, the evaluation of the synergic effects of the UV/O_3+S process were investigated and discussed.
The experimental activity, which was carried out in the second part of the research, pursued the following objectives:

- the continuous toluene abatement performance of a conventional bacterial BTF and an innovative tubular algal-bacterial photobioreactor (TPBR);
- the influence of the empty bed residence time (EBRT) and the toluene inlet concentration on pollutant biodegradation in both bioreactors;
- the determination of the limiting stage under the multiple operational conditions and the evaluation of the capacity of the bioreactors to cope with toluene surge;
- the assessment of the dynamics of the microbial communities in both bioreactors.

With a view at gradually increase the inlet loads entering the bioreactors, the EBRT was gradually decreased from 2 minutes to 45 seconds and the toluene inlet concentrations were gradually increased from 150 to 300 mg m^{-3}.
Toluene mass transfer tests and a final robustness test were carried out in order to determine the process stability towards inlet load fluctuation and the limiting factor (mass transfer or microbial activity).
The changes in microbial community were also determined using molecular biology techniques.

7. Materials and methods

This chapter describes experimental setups and analytical methods adopted to carry out the research.

To this end, it is divided in two main sections:

- the first one is focused on the materials, devices, experimental set-up and methods used for the evaluation of the performances of the integrated process of UV- Ozonation, and its combination with the absorption for the abatement of the model VOC;
- the second section describes materials, devices, experimental set-up and methods used for the comparative evaluation of BTF and TPBR for the continuous abatement of the model VOC.

The experimental activity has been carried out at the Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering of Salerno University (Italy) and at the Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain).

7.1 UV/O_3 and UV/O_3+S systems

Research studies of the first phase were carried out at the Sanitary Environmental Engineering Division (SEED) Laboratory of the Department of Civil Engineering of the University of Salerno.
In order to compare UV/O_3 and UV/O_3+S effectiveness as VOCs removal treatment technologies, the variation in both removal yields and residue ozone was evaluated.
In particular, experimental activity first focused on the definition of the optimal operating conditions for the single-stage treatment.
Subsequently, the integration with an additional wet scrubbing treatment was evaluated.
All tests were performed in triplicate and the inlet toluene concentrations and the applied voltage were systemically varied, with a view at pointing out the single

effects of absorption and oxidation processes in toluene elimination capacity, along with their synergisms.

7.1.1 Chemicals

Toluene (CAS No 108-88-3) was purchased from Sigma Aldrich with a purity of 99.9% and used for the generation of the synthetic gaseous stream (Table 7-1). Potassium iodide (CAS No. 7681-11-0, VMR Chemicals), sulfuric acid (CAS No. 7664-93-9, Carlo Erba), starch paste (CAS No. 9005-84-9, Carlo Erba Reagent) and sodium thiosulfate (CAS No. 10122-17-7, Carlo Erba Reagents) were used for the determination of ozone concentration.

Table 7-1: Toluene (CAS No 108-88-3) characteristics

Parameter	Value
Vapor density	3,2 (vs air)
Vapor pressure	22 mmHg (20°C)
Vapor pressure	26 mmHg (25°C)
Assay	≥ 99,5%
Form	liquid
Autoignition temperature	997°F
Shelf life	≈ 3 years
Impurities	≤ 0,003% S compounds ≤ 0,030% water

7.1.2 Experimental set-up and operating procedure

The pilot-scale plant was composed by a system for the generation of the synthetic gaseous contaminated stream, the UV/O_3 reactor and the scrubbing unit. Figure 7-1 shows the scheme of the experimental set-up.

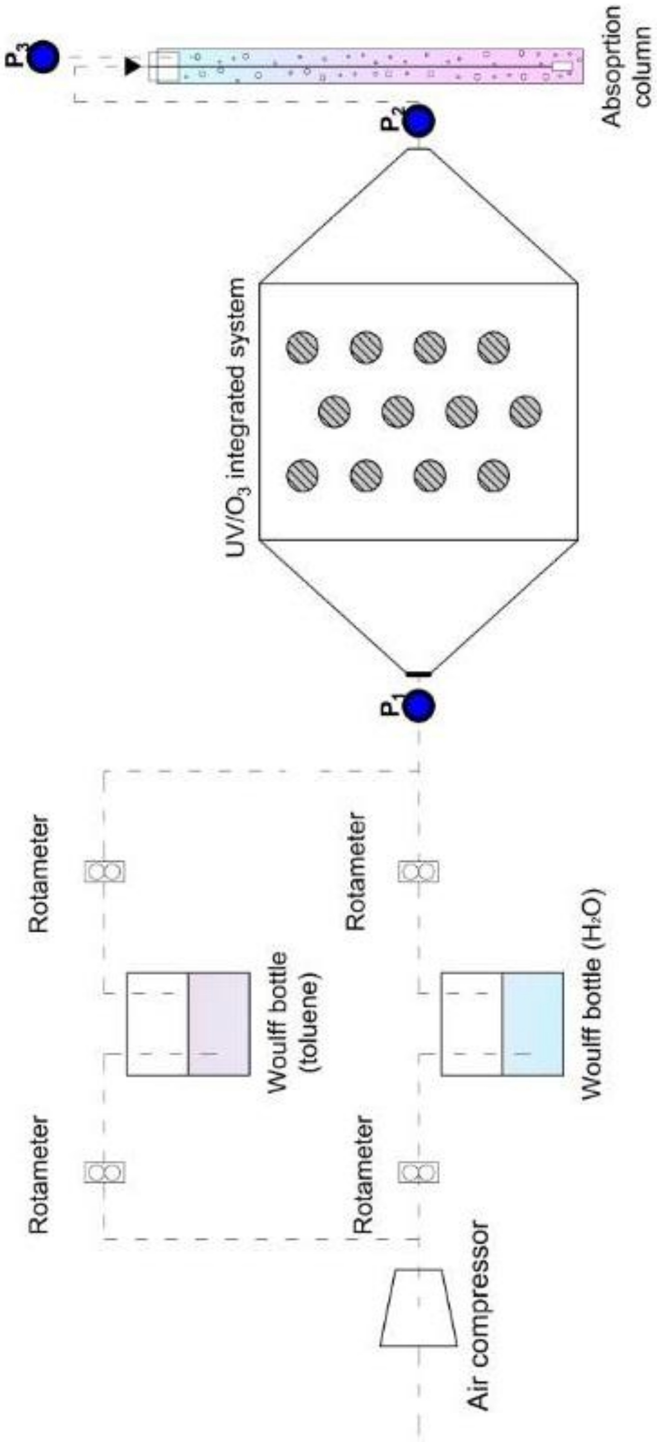


Figure 7-1: Scheme of the Experimental Set-Up of UV-O_3 reactor

The generation of the synthetic contaminated gaseous stream was obtained by a metered flow of oil-free compressed air forced to pass through a Woulff-bottle pure toluene containing.

This concentrated vapor was diluted to the expected concentration with oil-free water-saturated compressed air (Z. Wang et al., 2013c). Temperature control was provided by a thermostatic bath maintained at 28°C ± 10°C (Lab Instruments). Humidified air and toluene-rich air then merged into a tubing before entering the reactor.

The UV/O_3 reactor (Figure 7-2) was developed by the SEED research group and consists in a steel photo-reactor composed of a central body (48.6 cm length x 33.7 cm height x 17.8 cm width), which contains four ozone-generating UV lamps (Figure 7-3) (PROCOMAT), and two pyramidal-truncated hoods (25 cm height). Each lamp has a rating of 14 watts and with a length of 28.7 cm (*Table* ***7-2***). An additional stage of water scrubbing was also investigated.

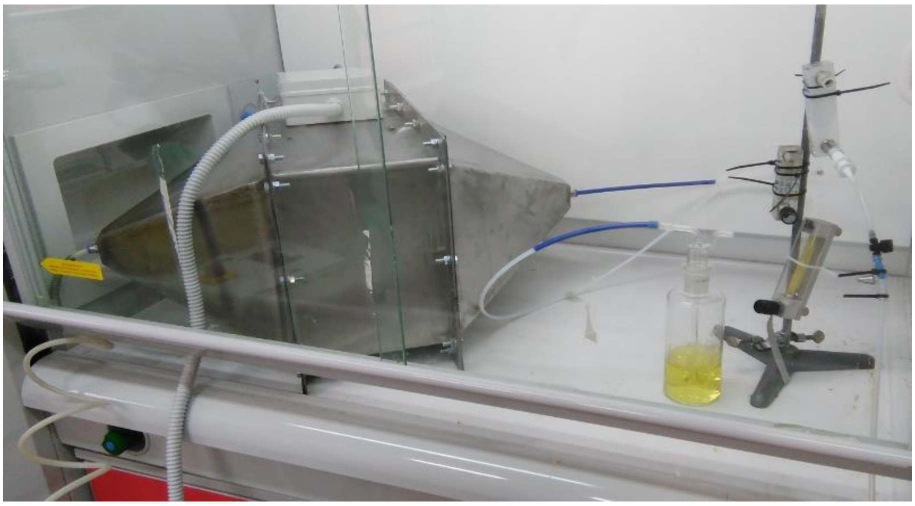


Figure 7-2: UV/O_3 reactor

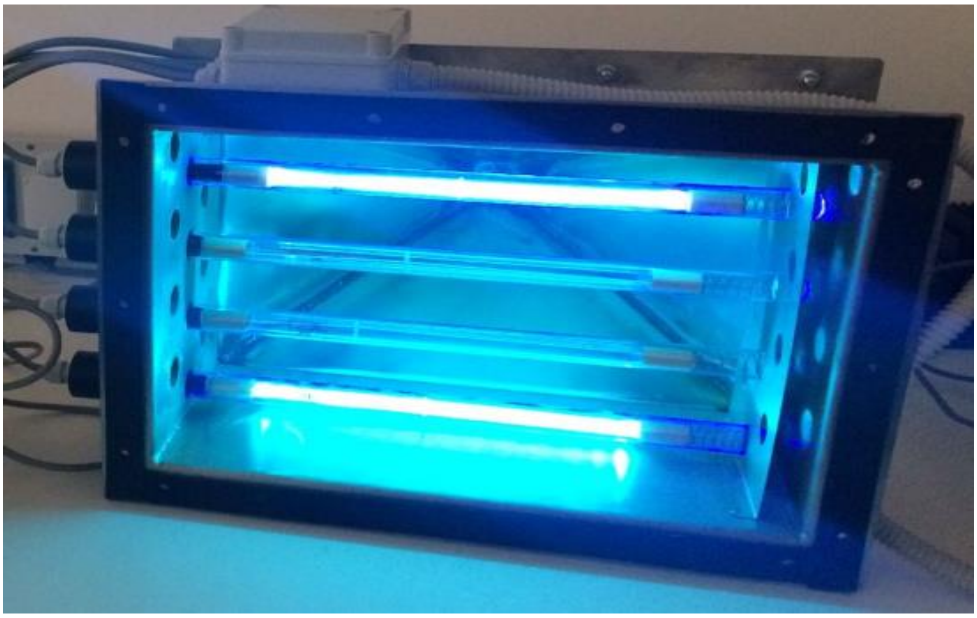


Figure 7-3: UV lamps configuration

Table 7-2: UV lamps characteristics

Parameters	Value
Lamp Wattage	14 W
Lamp Current	425 mA
Lamp Voltage	34 V

Outlet air from the stainless reactor was dispersed in the absorption unit by a metallic diffuser.

The analyses were carried out at 3 points, identified as P_1, P_2 and P_3, representing the inlet and outlet gas streams of the investigated systems.

Two configurations were analyzed for each test, the UV/O_3 oxidation and the upgraded system with the scrubbing unit.

For each configuration, different tests were performed by changing the main operational parameters. The flow rate of humidified air was fixed at 15 L min^{-1} and toluene enriched air was varied to achieve the desired inlet concentrations.

Ozone dosage was varied based on the number of lamps switched on.

Before each test, the reactor and the lamps were cleaned by purging with clean air for 15 minutes.

7.1.3 Analytical methods

Toluene concentration in the gas phase was measured using a GC-PID (Photoionization Detector, Tiger, Ion Science).

Produced ozone and ozone residual from the stand-alone and the combined processes were measured using the Standard Method 2350E 106 (Ozone Demand/Requirement Semi Batch Method). The ozone titration procedure is reported in Figure 7-4.

$$O_3(\text{mg min}^{-1}) = \frac{V \cdot N \cdot 2400}{t} \tag{1}$$

Where:

- V is the volume of the thiosulfate used for the chemical titration;
- N is the normality;
- t is the time in minutes.

Figure 7-4: Ozone titration

7.1.4 Performance analysis

Performance studies were carried out analyzing the effects of the variation of the toluene inlet concentration and ozone dosage.

Toluene concentration was varied by adjusting the air flow outlet the toluene evaporator, which enter the reactor. Ozone production resulted dependent on the applied voltage, based on the number of lamps switched on. Each lamp has a potential equal to 34 V. The performances of the investigated processes were evaluated through the following parameters: removal efficiency (RE), elimination capacity (EC) compared to inlet load (IL) and residual ozone (RO).

$$RE\ (\%) = \frac{C_i - C_o}{C_i} \cdot 100$$

$$IL = \frac{Q \cdot C_i}{V}$$

$$EC = \frac{Q\ (C_i - C_o)}{V}$$

$$RO(\%) = \frac{O_{3,R}}{O_{3,P}} \cdot 100$$

Where:

- Ci and Co denote the inlet and outlet concentrations of toluene in ppm, respectively;
- Q is the air flow rate;
- V is the volume of the reactor;
- $O_{3,P}$ and $O_{3,R}$ are the produced and residual ozone.

7.2 BTF and TPBR

Research studies of the second phase were carried out at the Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain).

In order to systematically compare BTF and TPBR effectiveness as VOCs removal treatment technologies, the variation in both removal yields and carbon dioxide production were evaluated.

In particular, experimental activity focused on the definition of the adaptability of the processes towards inlet loads fluctuations, the optimal operating conditions for the single-stage treatment.

Subsequently, the integration with an additional wet scrubbing treatment was evaluated.

All tests were performed in triplicate and the inlet toluene concentrations and the applied voltage were systemically varied, with a view at pointing out the single effects of absorption and oxidation processes in toluene elimination and their synergism.

7.2.1 Inoculum

Activated sludge from Valladolid wastewater treatment plant (Spain) was used as bacterial inoculum for both bioreactors. The inoculum of the BTF was prepared using 0.5 L of the activated sludge, centrifuged for 10 min at 10000 rpm and resuspended in 250 mL of fresh mineral salt medium (MSM) at a final total suspended solids (TSS) concentration of 5160 mg L^{-1}.

The TPBR was inoculated with 0.5 L of the activated sludge (prepared as above described), and 1.2 L of microalgae culture (from a high rate algal pond (HRAP) operated in the Environmental Technology Group at University of Valladolid, Spain), centrifuged for 10 min at 10000 rpm and resuspended in 500 mL of fresh MSM at a final TSS concentration of 5940 mg L^{-1}.

7.2.2 *Chemicals and mineral salt medium*

The MSM used for BTF and TPBR operation was composed of (g L^{-1}): Na_2HPO_4 (2.44); KH_2PO_4 (1.52); NH_4SO_4 (1); $MgSO_4 \cdot 7H_2O$ (0.2) and $CaCl_2 \cdot 2H_2O$ (0.05) and 10 mL L^{-1} of SL-4 stock solution containing: EDTA (0.5 g L^{-1}) and $FeSO_4 \cdot 7H_2O$ (0.2 g L^{-1}) and 100 mL L^{-1} of SL-6 stock solution composed of (g L^{-1}) $ZnSO_4 \cdot 7H_2O$ (0.1); $MnCl_2 \cdot 4H_2O$ (0.03); H_3BO_3 (0.3); $CoCl_2$ (0.2); $CuCl_2 \cdot 2H_2O$ (0.01); $NiCl_2 \cdot 6H_2O$ (0.02); $Na_2MoO_4 \cdot 2H_2O$ (0.03). Toluene was purchased from PANREAC (Barcelona, Spain) with a purity of 99.8%.

7.2.3 *Experimental set-up and operating procedure*

The BTF consisted of a cylindrical jacketed PVC column with an inner diameter of 0.08 m and a height of 0.79 m Figure 7-1.

The column was packed with plastic Kaldnes rings (Evolution Aqua, United Kingdom) at a working volume of 4 L. The recirculation of MSM was carried out by a peristaltic pump (Watson-Marlow 520S IP31) from an external 1.2 L jacketed holding tank stirred at 400 rpm (Agimatic-S, Selecta®, Spain).

The MSM was continuously recycled counter-currently from the top to the bottom of the column at a trickling liquid velocity (TLV) of 2 m h^{-1}. The synthetic toluene-laden emission was supplied from the bottom of the BTF.

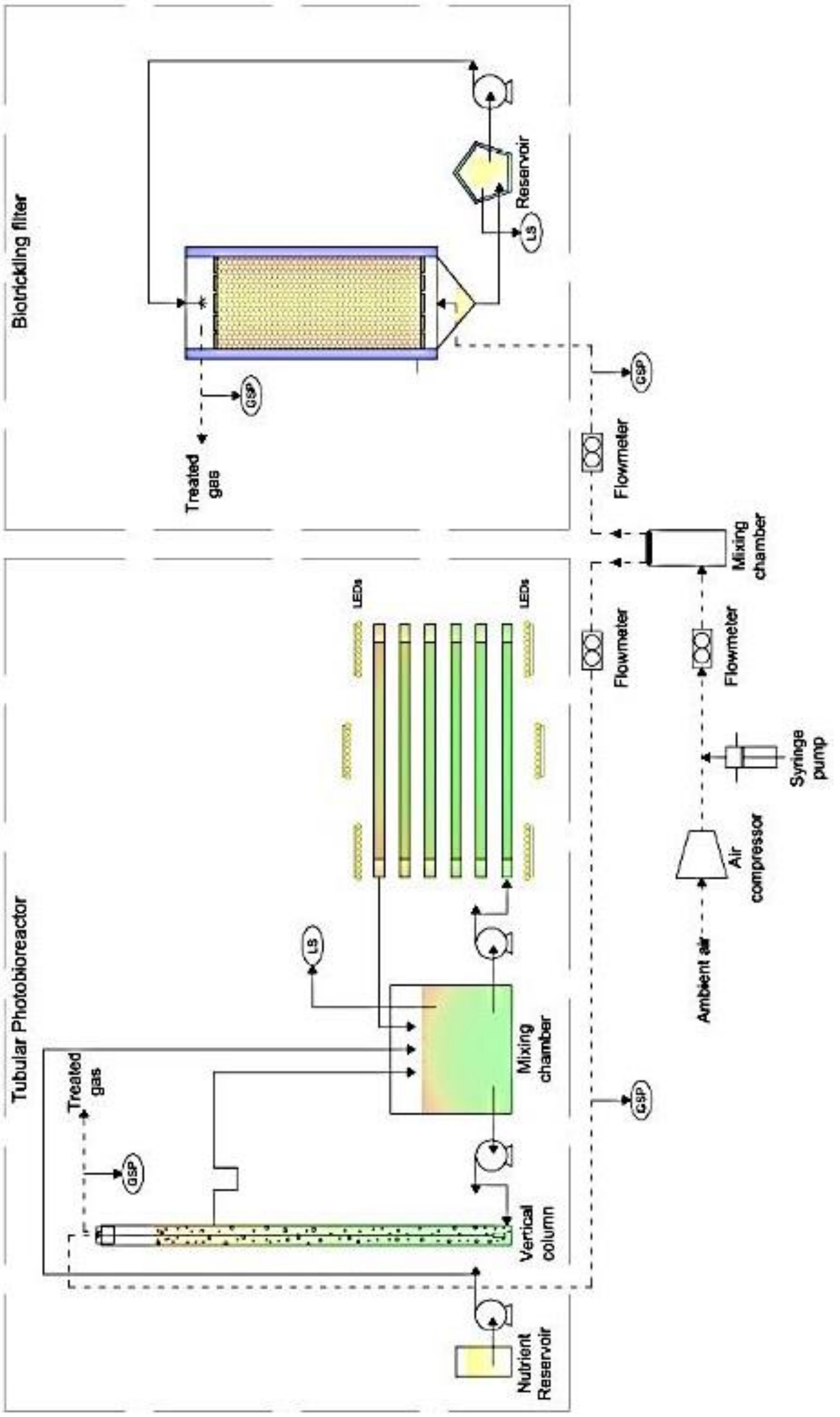


Figure 7-5: Scheme of the experimental set-up of TPBR and BTF

Figure 7-6: Biotrickling filter

The 45.6 L TPBR consisted of tubes with an internal diameter of 5 cm and a total length of 20 m. The TPBR was interconnected, via liquid recirculation, to a 2 L vertical absorption column (AC, height = 120 cm, inner diameter = 4.5 cm) and a 70 L mixing chamber (44 cm × 33 cm × 49 cm).

The cultivation broth was recirculated through the TPBR tubes at a linear velocity of 0.53 m s^{-1}, while the liquid to gas flow rate ratio (L/G) in the AC was set at 0.5. Cool white light emitting diodes (LEDs) were arranged vertically at both sides of the TBPR and configured with a 12:12 h:h light-dark illumination regime.

Figure 7-7: Tubular Photo-Bioreactor

Figure 7-8: Absorption Column

The synthetic toluene-laden emission was supplied via a metallic diffuser (located at the bottom of the AC) co-currently with the algal-bacterial cultivation broth recirculated from the mixing chamber.

The synthetic polluted stream was obtained by injecting pure liquid toluene at a specific flow rate directly into the inlet compressed air line by means of a syringe pump (Fusion 100, Chemyx Inc. USA). The resulting gas stream was divided into two streams using gas flow rotameters (Aalborg, USA) prior feeding the bioreactors.

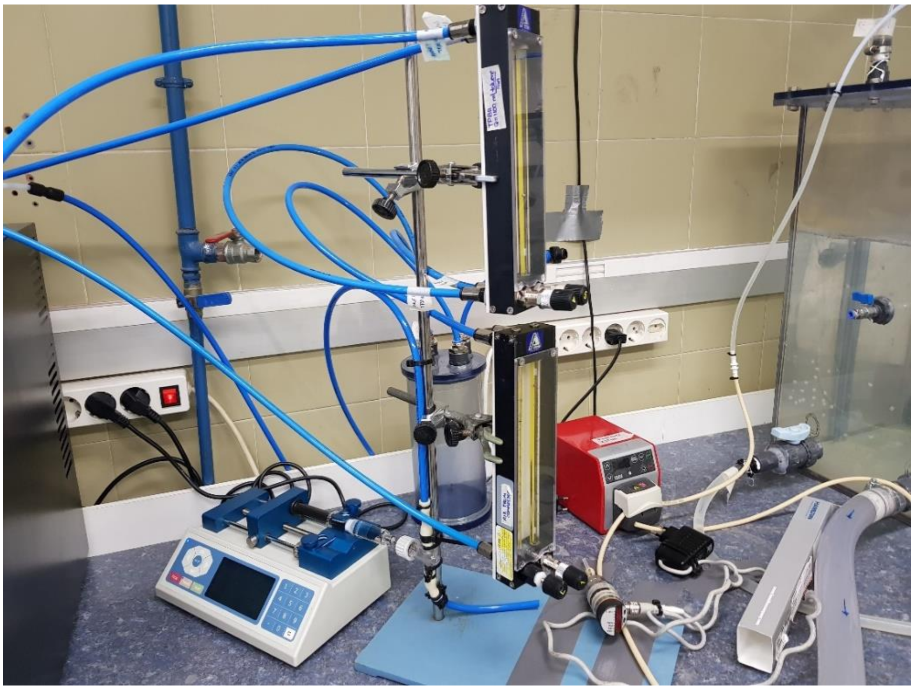


Figure 7-9: Synthetic gas stream generation system

The systems were operated for 90 days testing four different operating conditions, gradually increasing the inlet load (IL) (Table 7-3). The EBRT was fixed at 2 min during stage I, and subsequently decreased, varying the gas flowrate (Q), to 1 and 0.75 min in stages II and III-IV, respectively.

During stages I-III, toluene inlet concentration was set at 150 mg m^{-3}, and increased to 300 mg m^{-3} during stage IV. From day 0 to 13 (stage I), 200 mL of the cultivation broth were daily exchanged with fresh MSM. The MSM renewal rate was subsequently increased to 400 (stages II-III), 800 (stage IVa) and 1600 mL d^{-1} (stages IVb-IVc).

The pH of the fresh MSM daily exchanged in the BTF was manually adjusted at 8.5 (by addition of a NaOH solution 5 M) from day 74 onwards. No chemicals were added to control the pH in the TPBR. Finally, the light intensity in the TPBR was adjusted at ~50 µmol m^{-2} s^{-1} during the first 74 days and increased afterwards at ~150 µmol m^{-2} s^{-1}.

Inlet and outlet toluene, CO_2, N_2 and O_2 concentrations in the gas phase, and pH and dissolved oxygen (DO) in the cultivation broth of the bioreactors were daily analyzed. Liquid samples for the determination of the concentration of total organic carbon (TOC), total nitrogen (TN), nitrite and nitrate were taken three times per week.

Samples of the inoculum and the cultivation broth at the end of each operating stage in the TPBR and of the inoculum and the biofilm at the end of the experimental period in the BTF were drawn to carry out a characterization of the microalgae and/or bacterial population structure.

Table 7-3 – Operating parameters during the different operational stages in the BTF and the TPBR

Stage	**I**	**II**	**III**	**IVa**	**IVb**	**IVc**
Days	*0-13*	*14-37*	*38-58*	*58-69*	*70-74*	*75-83*
IL_{BTF} (g m^{-3} h^{-1})	4.5	9	12	24	24	24
IL_{TPBR} (g m^{-3} h^{-1})	4.95	9.9	13.2	26.4	26.4	26.4
EBRT (min)	2	1	0.75	0.75	0.75	0.75
Q_{TPBR} (mL min^{-1})	1100	2200	2933	2933	2933	2933
Q_{BTF} (mL min^{-1})	2000	4000	5333	5333	5333	5333
Toluene inlet concentration (g m^{-3})	0.15	0.15	0.15	0.3	0.3	0.3
MSM renewal rate (mL d^{-1})	200	400	400	800	1600	1600
BTF pH control	No	No	No	No	No	Yes
TPBR light intensity (µmol m^{-2} s^{-1})	~50	~50	~50	~50	~50	~150

Samples of the inoculum and the cultivation broth at the end of each operating stage in the TPBR and of the inoculum and the biofilm at the end of the experimental period in the BTF were drawn to carry out a characterization of the microalgae and/or bacterial population structure.

7.2.4 Mass transfer and robustness tests

A mass transfer test was performed under steady state condition in each operational stage in order to elucidate whether bioreactors performance was limited by mass transfer of toluene from the gas to the liquid phase or by microbial activity. For this purpose, inlet toluene concentration was increased by a factor of ~3 for 5 hours, hourly monitoring the inlet and outlet toluene and CO_2 gas concentrations. This increase in the inlet toluene concentration resulted in a higher gas-liquid concentration gradient and therefore in a proportional increase in the amount of toluene potentially transferred to the liquid phase according to the Fick's law:

$$F_i = K_L a \left(\frac{C_{i,G}}{H} - C_{i,L} \right) \qquad 6)$$

Where:

- F_i is the volumetric toluene mass transfer rate (g m^{-3} h^{-1});
- $K_L a$ is the overall volumetric mass transfer coefficient (h^{-1});
- $C_{i,G}$ and $C_{i,L}$ are the toluene concentrations in the gas and liquid phases (g m^{-3});
- H is the Henry's Law constant.

In this context, an increase in the EC and the PCO_2 when increasing toluene IL would indicate that process performance was mass transfer limited. On the contrary, similar ECs and PCO_2 than those corresponding to the preceding steady state would indicate biological limitation.

A robustness test in both bioreactors was also carried out by the end of the experiment. Toluene feeding was switched off for 3 days in order to simulate typical operating conditions in a manufacturing plant (air extraction shutdown during the weekend). Inlet and outlet toluene and CO_2 gas concentrations and pH in the liquid media were measured hourly for the first 5 hours following toluene feed resumption, and then twice a day until stabilization.

7.2.5 Analytical methods

Toluene gas concentrations were analyzed in a Bruker 3900 gas chromatograph (Palo Alto, USA) equipped with a flame ionization detector and a Supelco Wax (15 m × 0.25 mm × 0.25 µm) capillary column. Oven temperature was initially maintained at 50 °C for 1 min, increased at 50 °C min^{-1} up to 70 °C and then at 65 °C min^{-1} to a final temperature of 140 °C. N_2 was used as the carrier gas at 1 mL min^{-1}. CO_2, N_2 and O_2 gas concentrations were determined in a Bruker 430 gas chromatograph (Palo Alto, USA) coupled with a thermal conductivity detector and equipped with a CP-

Molsieve5A (15 m × 0.53 m × 15 m) and a P-PoraBOND Q (25 m × 0.53 m × 10 m) columns. The oven, injector and detector temperatures were maintained at 40, 150 and 175 °C, respectively. Helium was used as the carrier gas at 13.7 mL min^{-1}. Gas sample injections were carried out with a 100 µl gas-tight glass syringe (Hamilton, USA).

DO concentration in the culture broth of the TPBR was monitored by an OXI 330i oximeter (WTW, Germany). The pH of the liquid samples was determined by a Crison 50 12T pH meter (Crison Instruments, Spain). Biomass concentration was measured as TSS according to Standard Methods (American Water 167 Works Association, 2012). Samples for the determination of TOC and TN concentrations were filtered through 0.22 µm filters (Merck Millipore. USA) prior analysis in a TOC-VCSH analyzer (Shimadzu, Japan) coupled with a chemiluminescense detection TN module (TNM-1) (Shimadzu, Japan). Nitrite and nitrate concentrations in the liquid phase were analyzed via HPLC-IC using a Waters 515 HPLC pump coupled with a conductivity detector (Waters 432) and equipped with an IC-PAK Anion HC column (4.6 × 150 mm) and an IC-Pak Anion Guard-Pak (Waters). Samples were eluted isocratically at 2 mL min^{-1} (at room temperature) with a solution of distilled water/acetonitrile/n-butanol/buffer at 84/12/2/2% v/v.

7.2.6 DNA extraction, Illumina Library preparation and bioinformatic analysis

Biomass samples were drawn at different stages during the experimental period and stored at -20 ºC prior to sequencing microbial analysis: BTF_0_AS (activated sludge inoculum of the BTF), BTF_IV (end of operation of the BTF, stage IVc), TPBR_0_HRAP (microalgae inoculum of the TPBR), TPBR_0_MIX (activated sludge + microalgae inoculum of the TPBR), and TPBR_II, TPBR_III and TPBR_IV (end of stages II, III and IVc in the TPBR, respectively). DNA extraction was performed using the Fast DNA Spin kit for soil (MP Biomedicals, LLC) according to the manufacturer's instructions but optimizing the time for cell lysis and the time for optimal DNA binding to the silica matrix. DNA integrity was checked by agarose gel (1.2 % (w/v)) electrophoresis. DNA concentration was determined using a NanoDrop spectrophotometer (NanoDrop Technologies, 154 Wilmington, USA). The extracted DNA was stored at -20ºC prior to 16S rDNA amplicon sequencing analysis. An aliquot of 5 ng µL^{-1} of genomic DNA was used to initiate the library preparation protocol (16S rDNA gene Metagenomic Sequencing Library Preparation Illumina protocol). Primers for 16S rDNA amplification targeted gene V3 and V4 regions (Klindworth et al., 2013). Illumina adapter overhang nucleotide sequences were added to the gene-specific sequences. After 16S rDNA gene amplification, the multiplexing step was performed using the Nextera XT DNA Library Preparation Kit (Illumina, San Diego, CA) with a reduced number of PCR cycles (25) using 55º C as annealing temperature. 1 µl of the PCR product was run on a Bioanalyzer DNA 1000 chip to verify the size (expected size ~550 bp). After size verification the libraries were sequenced using a 2 × 300pb paired-end run (MiSeq Reagent kit v3 (Illumina, San Diego, CA)) on a MiSeq Sequencer according to manufacturer's instructions (Illumina). Sequencing analysis was carried out by the Foundation for the Promotion of Health and Biomedical Research of Valencia Region (FISABIO, Spain).

Quality assessment of sequencing data was performed using the PRINSEQ-LITE program (Schmieder and Edwards, 2011) applying the following parameters: minimum read length: 50, trimming quality right: 30; trimming quality type: mean; trimming quality window: 20. The sequence data was analyzed using qiime2 pipeline (Caporaso et al., 2010). After quality assessment, denoising, paired-end reads joining, and chimera depletion was performed using DADA2 pipeline (Callahan et al., 2016). Taxonomic affiliations were assigned using the Naive Bayesian classifier integrated in quiime2 plugins using the SILVA_release_132 database (Quast et al., 2013). Inverse Simpson (ID) and Shannon indexes (H) were calculated using the Vegan library version 2.3e1 (J. Oksanen, F.G. Blanchet, M. Friendly, R. Kindt, P. Legendre, D. McGlinn, P.R. Minchin, R.B. O'Hara, G.L. Simpson, P. Solymos, M.H.H. Stevens, E. Szoecs, 2017). The Krona hierarchical browser tool (Ondov et al., 2011) was used to represent relative abundances of the different taxa within the microbial communities in the analyzed samples. The 16S rRNA sequence data sets was deposited in the National Center for Biotechnology Information (NCBI) under the study (BioProject) PRJNA505981 (http://www.ncbi.nlm.nih.gov/bioproject/505981).

7.2.7 *Microalgae identification*

Samples for the analysis of microalgae population in the TPBR were withdrawn at the beginning of the experimental period and by the end of stages II, III and IVc, fixed with lugol acid at 5% and stored at 4 °C prior to analysis. The identification, quantification and biometry measurements of the microalgae assemblage at steady state were performed by microscopic examination (OLYMPUS IX70, USA).

8. Results and Discussion

In the following paragraphs, the discussion of the experimental activity results is provided.
To this end, this chapter is divided in two main sections:

- the first one is focused on the results of the comparative evaluation of UV/O_3 and UV/O_3+S systems effectiveness for the removal of VOCs;
- the second part discusses the comparative evaluation of BTF and TPBR for the continuous abatement of VOCs.

8.1 UV/O_3 and UV/O_3+S systems

8.1.1 Influence of inlet concentration

Figure 8-1 illustrates the effect of the increasing in inlet concentration on the degradation of toluene respectively for the UV-Ozone system (UV/O_3) under different ozone dosages while shows the results of the combined system UV/O_3+S.

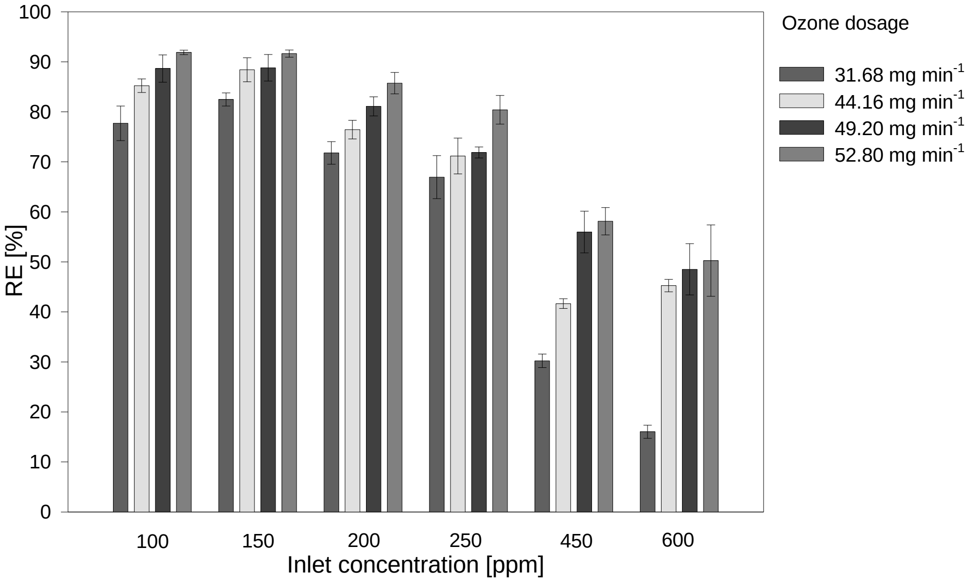


Figure 8-1: Influence of toluene inlet concentration on the Removal Efficiency (RE) under different ozone dosage applying the UV/O3 system

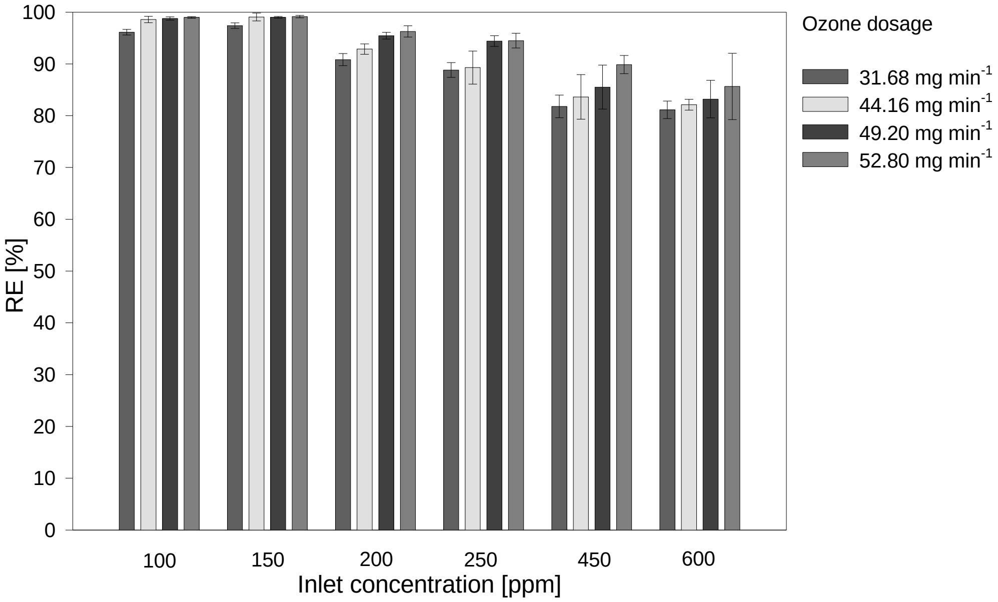


Figure 8-2: Influence of toluene inlet concentration on the Removal Efficiency (RE) under different ozone dosage applying the UV/O3+S system

Applying the lowest ozone dosage, the UV/O_3 system did not support an effective toluene removal for the highest inlet concentrations. The combined systems achieved, with the same ozone dosage, removal efficiencies higher than 80% for all the investigated inlet concentrations.

With the increase in concentration, applying the highest ozone dosages (44.16 and 52.80 mg min-1), it was observed that the stand-alone system still highlighted removal efficiency significantly reduced for the highest toluene inlet concentrations. This effect might be probably ascribable to the toluene accumulation and the simultaneous insufficiency of oxidants to support the degradation.

The forward reaction, resulting in the mineralization into carbon dioxide, was not favoured due to the limitation in terms of hydroxyl radicals (C. Y. H. Chao et al., 2007; Pengyi et al., 2003b; K.-P. Yu and Lee, 2007).

Removals up to 99% were obtained with the two-stage system. The higher performances of the combined system may be ascribable to the fact that the scrubbing phase promoted the solubilisation of the ozone and related by-products into the liquid phase; the residue ozone in the process water carried out a further oxidation of the contaminants transferred to this phase.

In Figure 8-3 and Figure 8-4 are reported the results in terms of residual ozone.

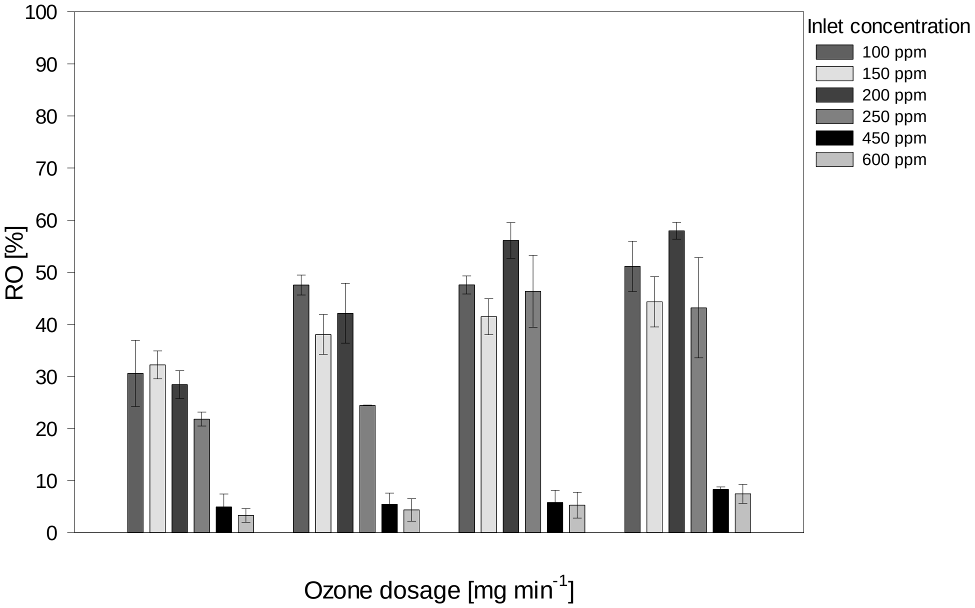


Figure 8-3: Influence of toluene inlet concentration on the residue ozone under different ozone dosage UV/O3 system

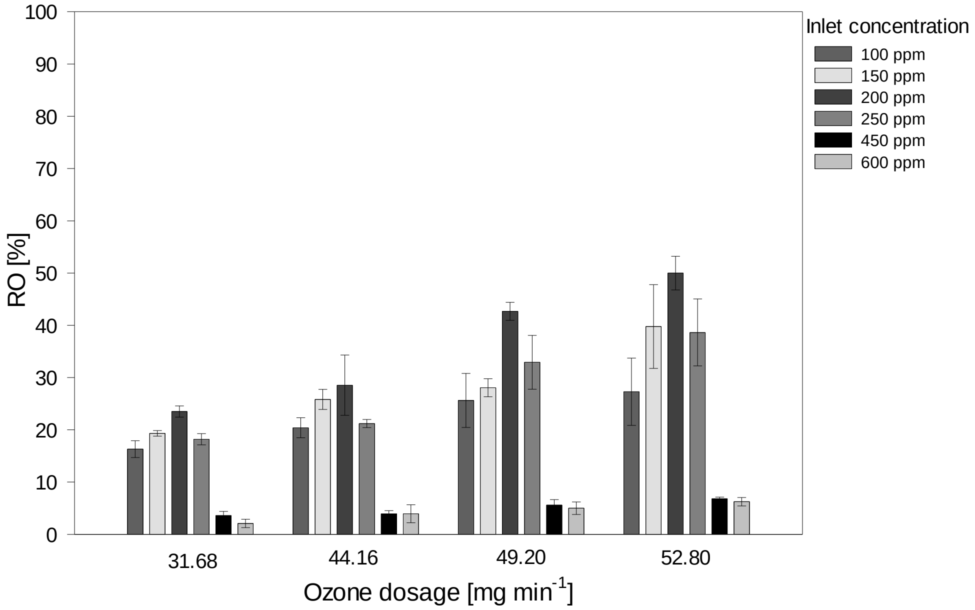


Figure 8-4: Influence of toluene inlet concentration on the residue ozone under different ozone dosage UV/O3+S system

With the increase in concentrations, the percentages of residual ozone tended to decrease. With an ozone dosage of 31.68 mg min^{-1} and an inlet toluene concentration of 600 ppm, the residual ozone resulted less than 3% for the combined process.

The presence of the scrubbing phase, indeed, supported an effective reduction of the residual ozone. This effect resulted more appreciable at lower inlet concentrations.

For all the investigated ozone dosages, at 450 and 600 ppm, the residual ozone resulted less than 10% for both investigated systems. The scrubbing process ensured a higher transfer of ozone into the liquid phase due to the high solubility of these compounds in water.

The presence of unreacted ozone and toluene was attributed to the faster reaction rate of ozone with hydroxyl radicals (5.3 x 10^{-11} cm^3 molecule^{-1} s^{-1}) compared to the reaction of ozone with toluene (1.2 x 10^{-20} cm^3 molecule^{-1} s^{-1}) (Z. Cheng et al., 2013; Ch. Subrahmanyam et al., 2010).

The excess ozone may scavenge the hydroxyl radicals, which reacted with O3 instead of toluene. These conditions probably led to the incomplete degradation of the pollutants.

At high ozone concentrations, it may be observed also a limiting reaction of UV with ozone for radical production. Higher ozone concentration limited the amount of highly reactive radicals and led to the formation of less reactive radicals as also observed by Cheng et al. (2013).

Other O_x-HO_x reactions of second-order, indeed, could also occur at high ozone concentrations, reducing the rate of oxidation (Johnson et al., 2014b).

8.1.2 Influence of ozone dosage

Ozone concentration resulted dependent on the applied voltage. An increase in the applied voltage resulted, obviously, into an increase in ozone dosage. Switching on one lamp (34 V) a corresponding ozone production of 31.7 mg min^{-1} was achieved.

Applying a voltage of 68 V, it was obtained an ozone dosage equal to 44.16 mg min-1. However, the increase in ozone dosage switching on from three (102 V) to four (136V) lamps resulted in the increase of ozone dosage from 49.2 to 52.8 mg min^{-1}.

The trend in the increase was, thus, not linear due to the configuration of the lamps in the reactor. The two lamps in the centre resulted directly invested by the airflow, but the other two located respectively at the top and bottom part of the reactor received less air flow and, consequently, contributed less to the ozone production.

In Figure 8-5 and Figure 8-6 are reported the results in terms of toluene reduction (ppm) varying the ozone dosage, for different inlet concentrations.

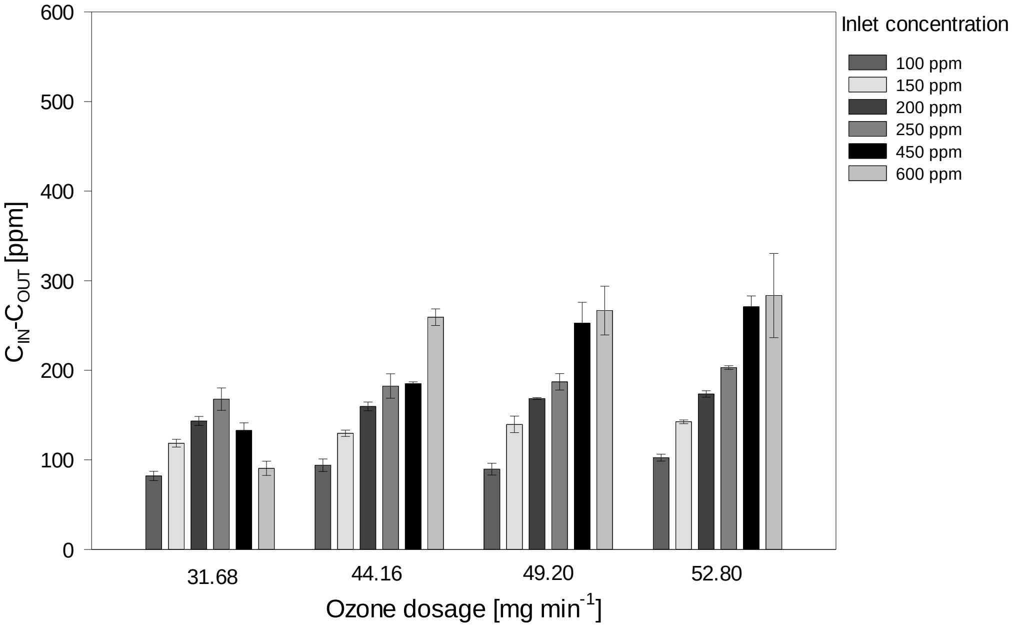


Figure 8-5: Influence of ozone dosage on the toluene abatement under different inlet concentrations applying the UV/O_3 system

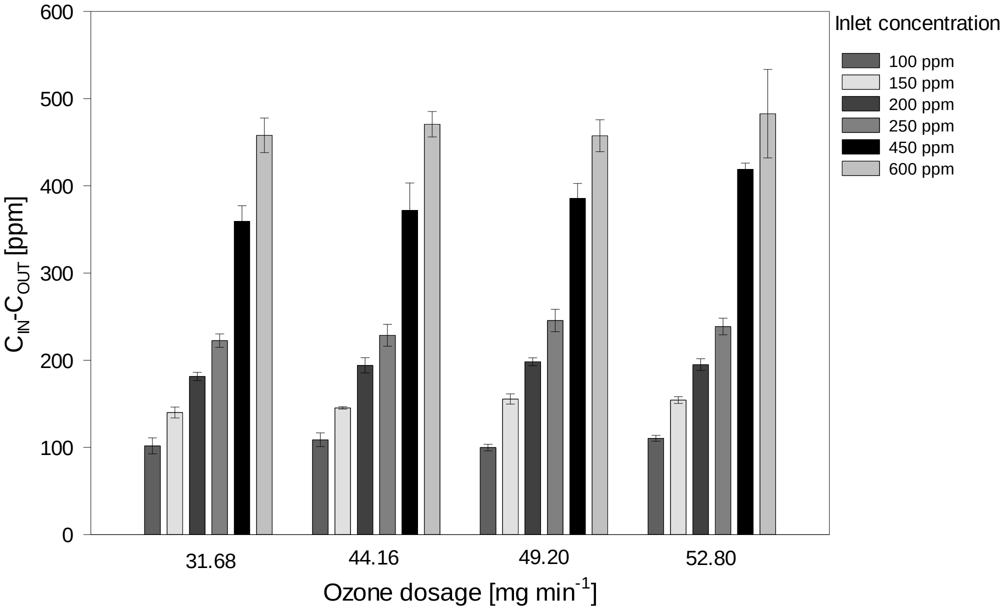


Figure 8-6: Influence of ozone dosage on the toluene abatement under different inlet concentrations applying the UV/O_3+S system

For the lowest inlet concentrations, the increase in ozone dosage did not significantly affected the reduction of toluene. Furthermore, the results of the stand-alone process resulted quite similar to the results of the combined systems.

The maximum toluene reduction for the UV/O_3 system at 100 ppm was achieved for the maximum ozone dosage and resulted equal to 102±4 ppm; at the same conditions, the combined system supported a toluene removal of 110±4 ppm.

For an inlet concentration of 150 ppm, the analysis of the reduction in toluene concentration highlighted the same behaviour. At an inlet concentration of 200 – 250 ppm, the effect of the increasing in the provided ozone started to be more appreciable.

At the same time, the combination with the scrubbing unit seemed to promote an enhancement of the performance, for each ozone dosage. At 450 ppm inlet toluene concentration, the eliminated toluene for the lowest ozone dosage resulted equal to 143±5 ppm for the single-step process, while the value providing the maximum ozone dosage reached 174±4 ppm.

The combined system allowed to achieve 195±6 ppm toluene removal for an applied a voltage producing 52.8 mg min-1of ozone. The toluene elimination increased with the increasing in toluene inlet concentration, a part from what observed for an ozone dosage of 31.68 mg min^{-1} in the single-stage reactor.

The results observed at these conditions may be probably due to an effect of toluene accumulation in the reactor. The maximum toluene elimination was achieved for an ozone dosage of 52.8 mg min^{-1} in the two-stage system and resulted equal to 483±51 ppm.

For the same operational parameters, the result achieved by the single-stage system was only 283±47 ppm. The ozone and oxidants in the aqueous phase did not represent a limiting factor for the oxidation process in the combined systems, differently by the conditions observed in the single-stage process.

A greater amount of ozone provided a higher quantity of oxidants for a more effective pollutant removal.

Based from the experimental data, for the lowest toluene inlet concentrations the effect of the increase in ozone dosage in the oxidation of toluene resulted marginal. This condition may be ascribed to the fact that toluene oxidation by hydroxyl radicals was the predominant mechanism in the process at these conditions. On the other hand, for higher inlet concentrations reactions of oxidants with toluene prevailed as major reaction pathways.

8.1.3 Comparative evaluation

In Figure 8-7 and Figure 8-8, it was compared the elimination capacity of both investigated system to the inlet load with a view at comparing the performances of the UV/O3 system and the combined system.

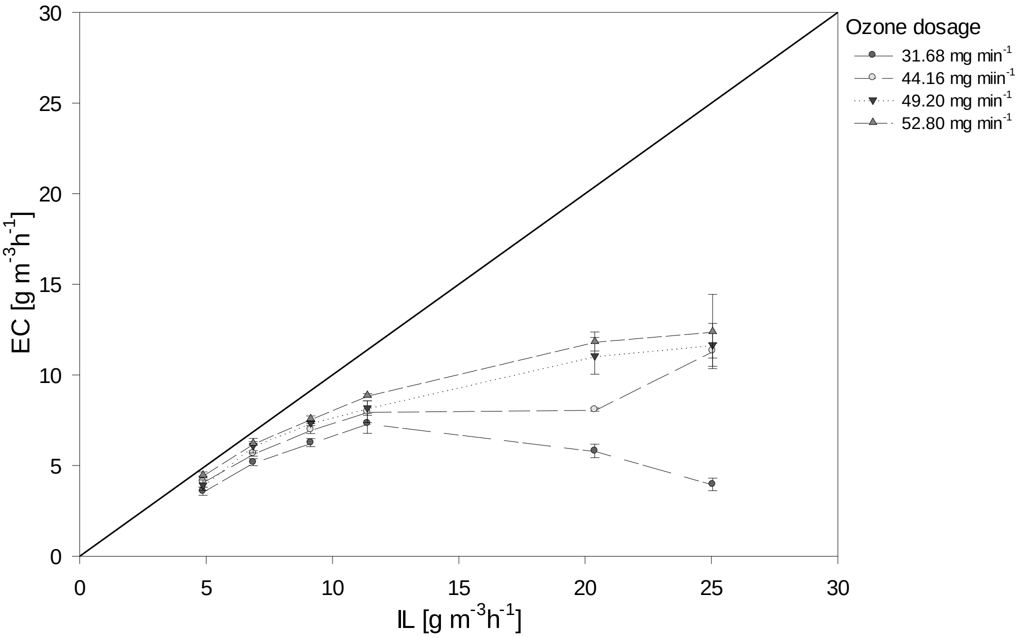


Figure 8-7: Inlet Load (IL) compared to Elimination Capacity (EC) applying the UV/O3+S system

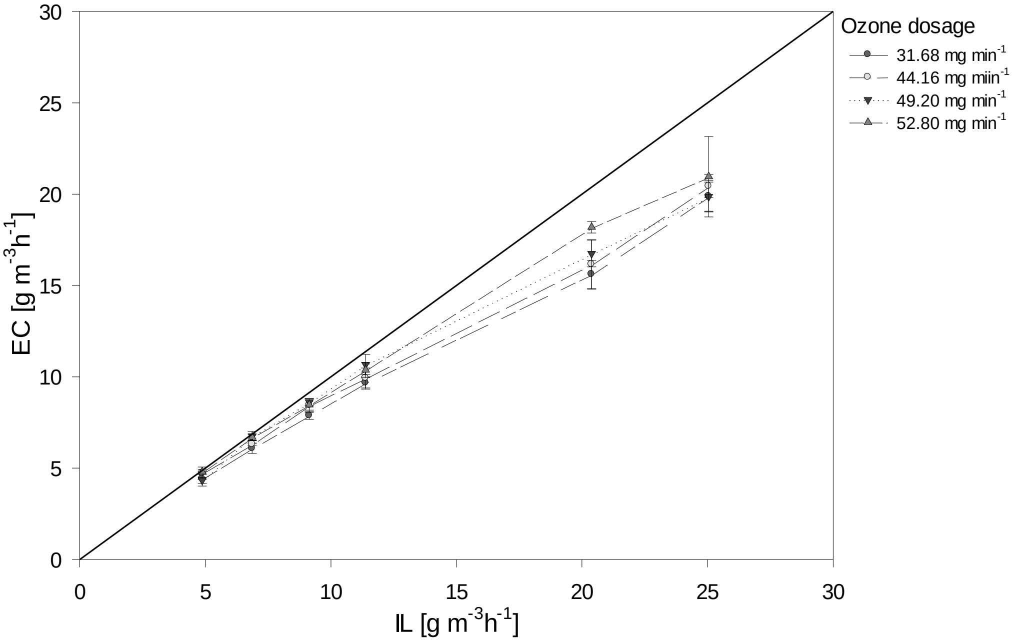


Figure 8-8: Inlet Load (IL) compared to Elimination Capacity (EC) applying the UV/O3+S system

The results highlighted UV/O_3+S process supported removal efficiencies closer to the ideal condition of 100% removal.

The comparison between the two graphs showed that applying the minimum ozone dose in the combined process were achieved higher treatment efficiencies than those obtained, at the maximum applied voltage, with the single-stage treatment. Increasing the inlet load, with the combined system the elimination capacities remained still close to the ideal condition. In UV/O_3 process, a significant reduction in toluene removal was observed for toluene inlet load higher than 10 g $m^{-3}h^{-1}$.

In the water scrubbing step, in fact, further degradation of unreacted toluene was due to absorption in the water phase and reaction with hydroxyl radicals from ozone decomposition. The scrubbing process provided a venue for the contact and oxidation by hydroxyl radicals in the liquid phase. Moreover, the scrubbing increased ozone consumption and lessened the exhaust ozone emissions.

8.2 BTF and TPBR

8.2.1 BTF performance

Toluene removal efficiency (RE) reached 92 % within the two first days of operation, which remained at average values of 90 ± 3 % during stage I.

This RE corresponded to steady state elimination capacities (ECs) of 4.1 ± 0.6 g $m^{-3}h^{-1}$ (Figure 8-9) and CO_2 production rates (PCO_2) of 10.6 ± 3.9 g $m^{-3}h^{-1}$ (Figure 8-10).

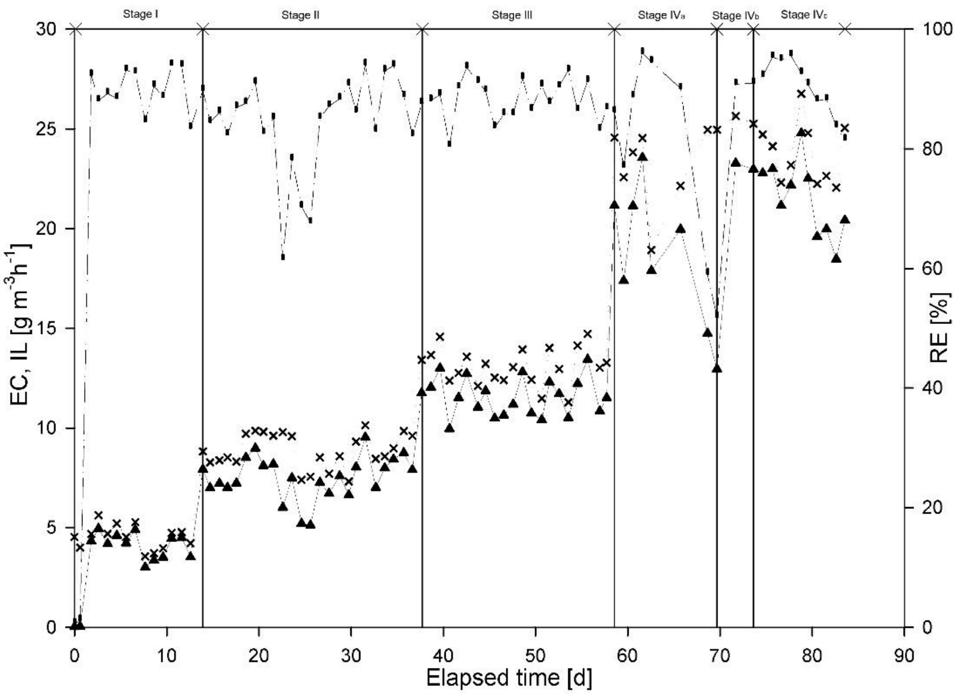


Figure 8-9: Time course of the toluene inlet load (···×···), elimination capacity (—▲—) and removal efficiency (--■--) in the biotrickling filter. Vertical lines separate different operating stages as indicated in the upper part of the graph.

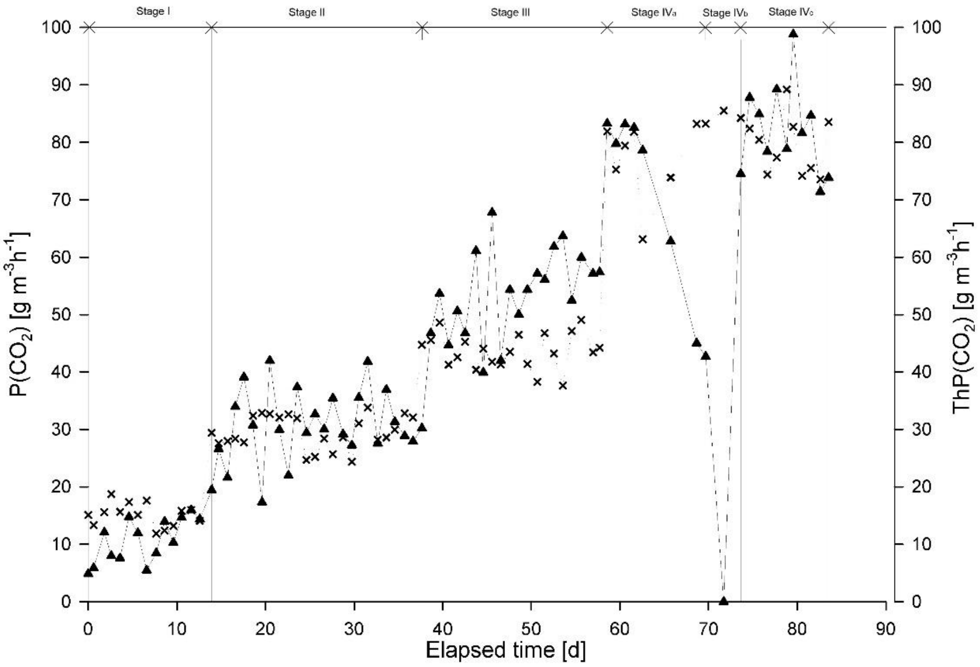


Figure 8-10: Time course of the real CO_2 production (PCO_2 —▲—) and the theoretical CO_2 production ($ThPCO_2$ ···×···) in the biotrickling filter. Vertical lines separate different operating stages as indicated in the upper part of the graph.

This PCO_2 was close to the theoretical CO_2 production ($ThPCO_2$), resulting in a toluene mineralization rate of ~71 %. The acidic metabolites resulting from microbial toluene biodegradation supported a decrease in the pH of the recycling media from 7.12 to 6.72 by day 13 (Figure 8-11).

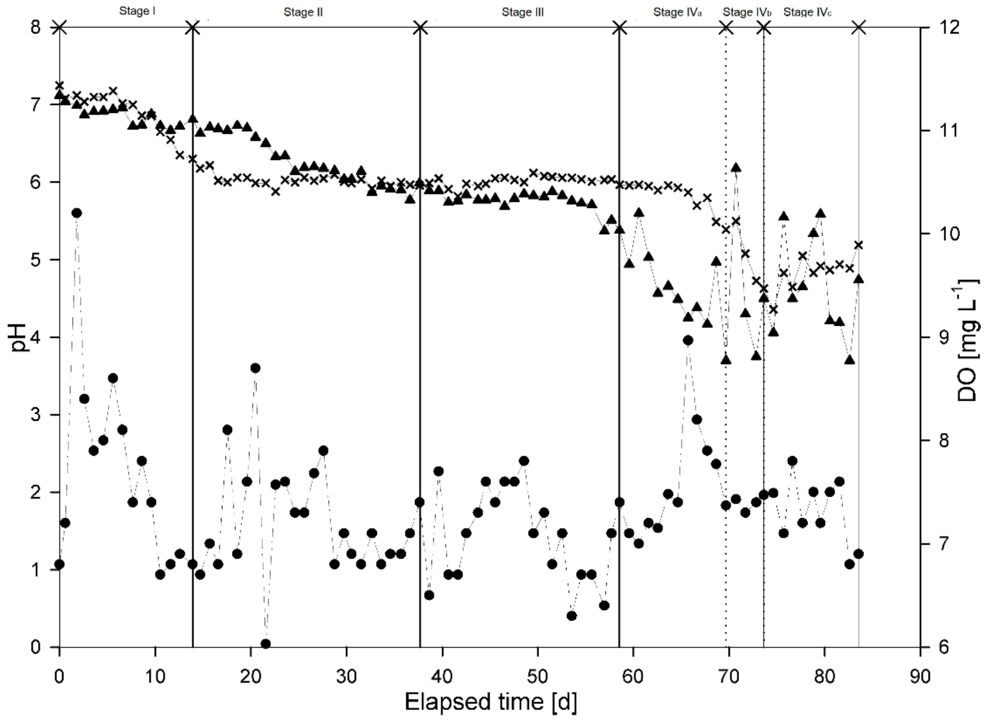


Figure 8-11: Time course of the pH in the BTF (—▲—) and in the TPBR (—×—), and dissolved oxygen in the TPBR (---●---). Vertical lines separate different operating stages as indicated in the upper part of the graph.

A toluene mass transfer test was carried out at the end of stage I (Figure 8-12). During the test, a ~3 times higher EC was recorded in the BTF when increasing the toluene IL, suggesting that the process was limited by toluene mass transfer from the gas to the liquid phase.

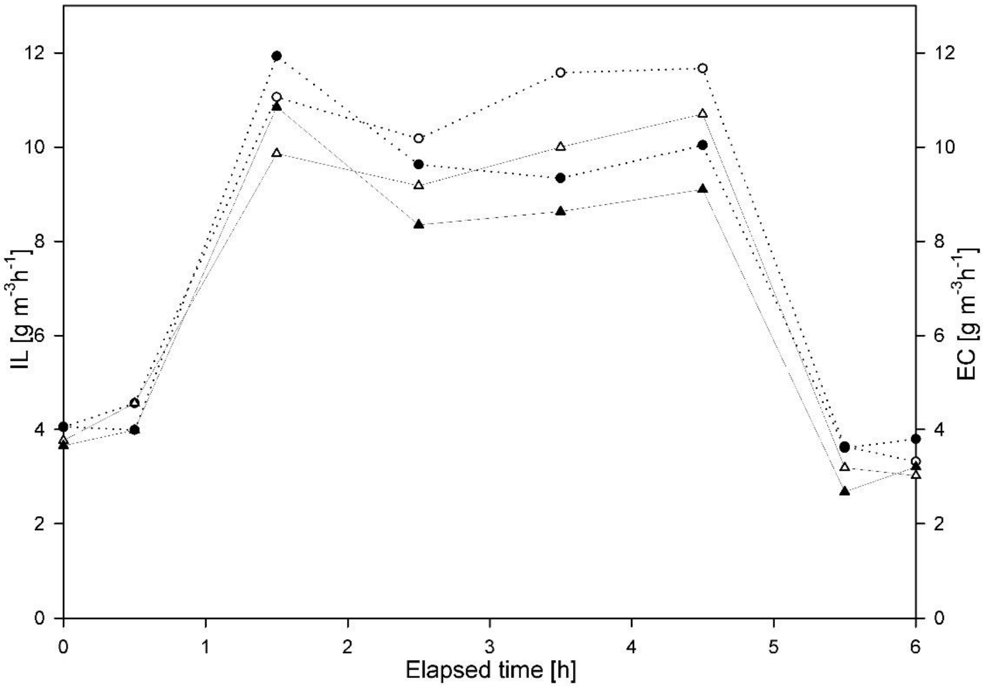


Figure 8-12: Time course of the Inlet load in the BTF (···●···) and the TPBR (···○···) and of the Elimination capacity in the BTF (—▲—) and the TPBR (—Δ—) during the mass transfer test performed between stages I and II

Then, the EBRT was reduced from 2 to 1 min by day 14, which corresponded to an increase in the inlet load up to 8.86 ± 0.86 g m^{-3}h^{-1}.

In this stage II, a drop in the RE to 61 % was observed by day 23 of operation, likely due to an accumulation of inhibitory intermediate metabolites as also observed in previous studies focused on the aerobic biodegradation of BTEX (El-Naas et al., 2014; Trigueros et al., 2010). Nevertheless, the system rapidly recovered former toluene abatement performance, reaching a stable EC of 7.49 ± 1.08 g m^{-3}h^{-1} (corresponding to average REs of 84 ± 8%) from day 27 onwards.

A mass transfer test was also conducted in stage II by increasing the IL from 9.6 ± 1.0 to 26.0 ± 1.2 g m^{-3}h^{-1}. The increase in the EC during this test up to a maximum EC of 23.22 g m^{-3}h^{-1} demonstrated that the system was limited by toluene mass transfer (Figure 8-13).

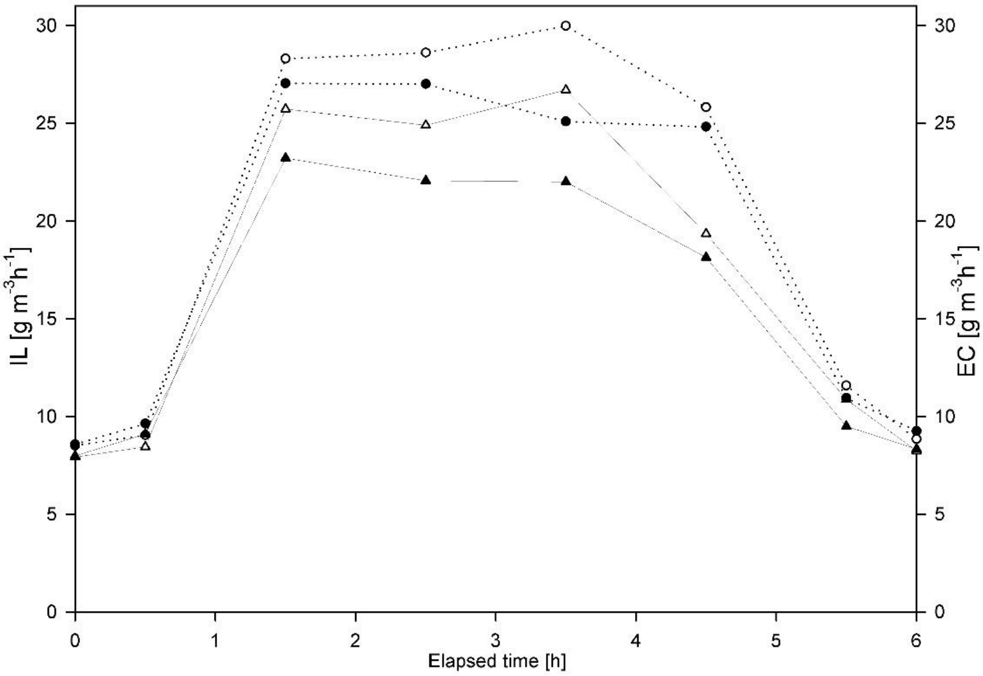


Figure 8-13: Time course of the Inlet load in the BTF (···●···) and the TPBR (···○···) and of the Elimination capacity in the BTF (—▲—) and the TPBR (—Δ—) during the mass transfer test performed between stages II and III

During stage III, an EBRT of 45 seconds and an inlet toluene concentration of 150 mg m^{-3} were set, resulting in an IL of 13.1 ± 0.9 g $m^{-3}h^{-1}$. The efficient toluene removal in the BTF during this stage was confirmed by an average EC of 11.6 ± 1.0 g $m^{-3}h^{-1}$ (RE of 88 ± 3%).

The increase in IL also resulted in a higher PCO_2 of 52.8 ± 8.9 g of CO_2 $m^{-3}h^{-1}$ that exceeded the theoretical CO_2 production (43.7 ± 3.1 g $m^{-3}h^{-1}$). This result was attributed to an active endogenous respiration of the bacterial community (Chen et al., 2010b; Cox et al., 1998). Gas-liquid mass transfer was also confirmed as the limiting factor also in this stage III (Figure 8-14).

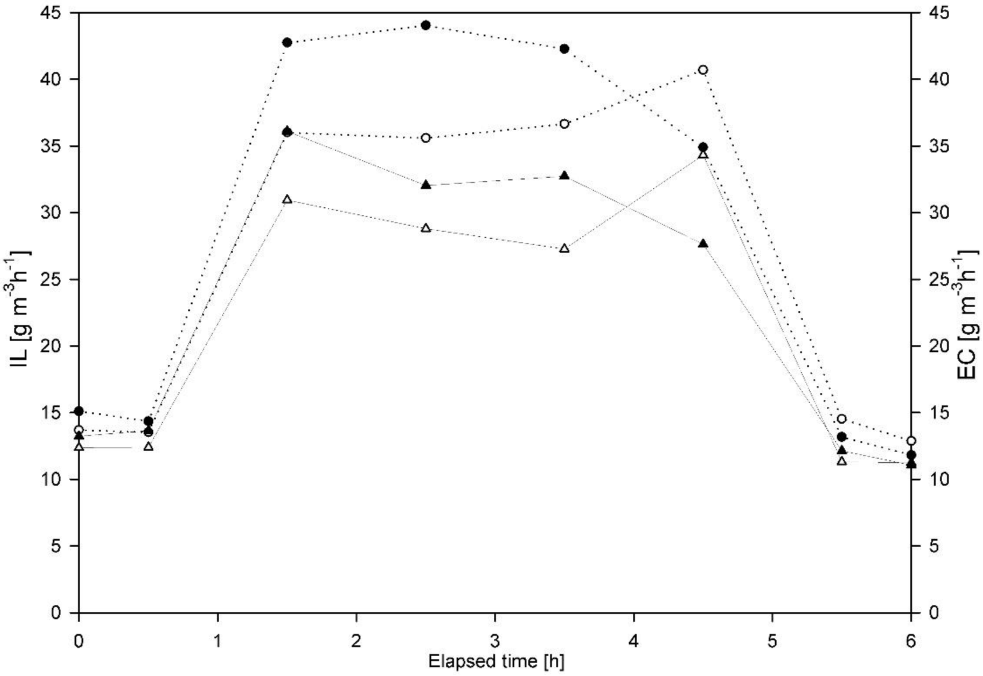


Figure 8-14: Time course of the Inlet load in the BTF (···●···) and the TPBR (···○···) and of the Elimination capacity in the BTF (—▲—) and the TPBR (—Δ—) during the mass transfer test performed between stages III and IV

During stage IV, the inlet concentration was doubled to 300 mg m^{-3} (average IL of 23.77 ± 1.76 g $m^{-3}h^{-1}$). The BTF initially supported an EC of 20.50 ± 3.02 g $m^{-3}h^{-1}$ of toluene (corresponding to a RE = 89 ± 7%) from day 59 to 66. However, a sharp drop in the toluene abatement performance was observed by day 69, when the RE decreased to 52%.

This decrease in toluene degradation resulted in a concomitant reduction in CO_2 production (Figure 8-9 and Figure 8-10), and was attributed to the acidification of the system derived from the accumulation of acidic metabolites. The progressive decrease in pH observed during this stage IVa (Figure 8-11), which likely inhibited microbial activity, confirmed this hypothesis (Song and Kinney, 2005).

In this context, the MSM renewal rate was increased by a factor of 2 (Stage IVb) in order to remove the toxic metabolites accumulated in the recycling medium. The increase in MSM renewal resulted in the rapid recovery of the RE and the concomitant increase in PCO_2.

However, a gradual decrease in the pH was again recorded from day 74 onwards, thus it was manually adjusted by increasing the pH of the fresh MSM up to 8.5 via NaOH addition in order to prevent a new reduction in the toluene EC (Stage IVc). During this last stage, the PCO_2 was slightly lower than the $ThPCO_2$ and the EC averaged 20.03 ± 3.47 g $m^{-3}h^{-1}$ (corresponding to a RE of 84 ± 15%). Finally, a mass transfer test was carried out to assess the capacity of the BTF to cope with toluene IL surges (Figure 8-15).

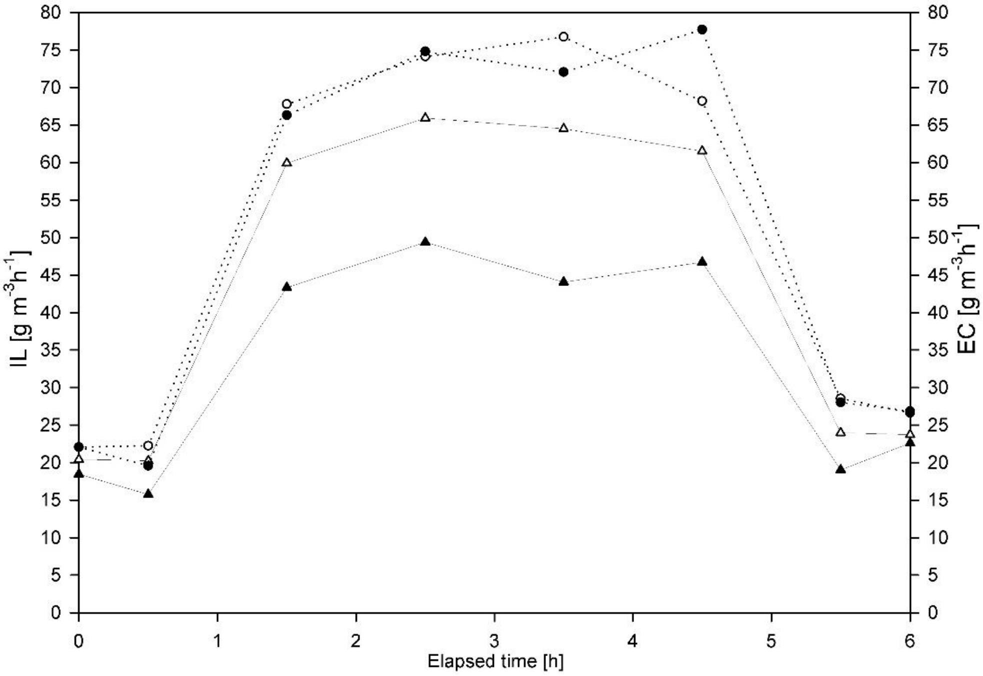


Figure 8-15: Time course of the Inlet load in the BTF (···●···) and the TPBR (···○···) and of the Elimination capacity in the BTF (—▲—) and the TPBR (—Δ—) during the mass transfer test performed by the end of stage IV

Despite the performance of the BTF was still limited by gas-liquid mass transfer, a lower EC increase was observed when increasing the IL (EC = 45.9 ± 2.8 g $m^{-3}h^{-1}$ at an IL of 72.7 ± 4.9 g $m^{-3}h^{-1}$).

8.2.2 TPBR performance

The TPBR rapidly achieved an average removal efficiency of 88 ± 3% during stage I, corresponding to an EC of 3.82 ± 0.94 g $m^{-3}h^{-1}$ (at an IL = 4.59 ± 0.57 g m^{-3} h^{-1}) (Figure 8-16).

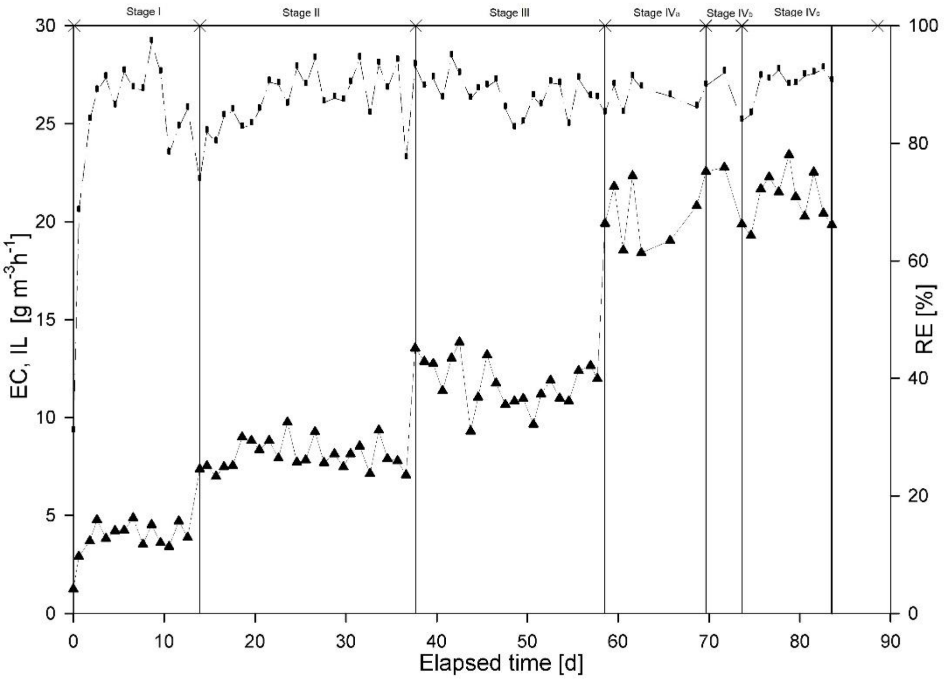


Figure 8-16: Time course of the toluene inlet load (···×···), elimination capacity (—▲—) and removal efficiency (--■--) in the tubular photobioreactor. Vertical lines separate different operating stages as indicated in the upper part of the graph.

Despite the fact that the TPBR supported an effective toluene degradation activity, the outlet CO_2 gas concentrations recorded were lower than the inlet concentrations as a result of microalgae photosynthetic CO_2 fixation (Figure 8-17).

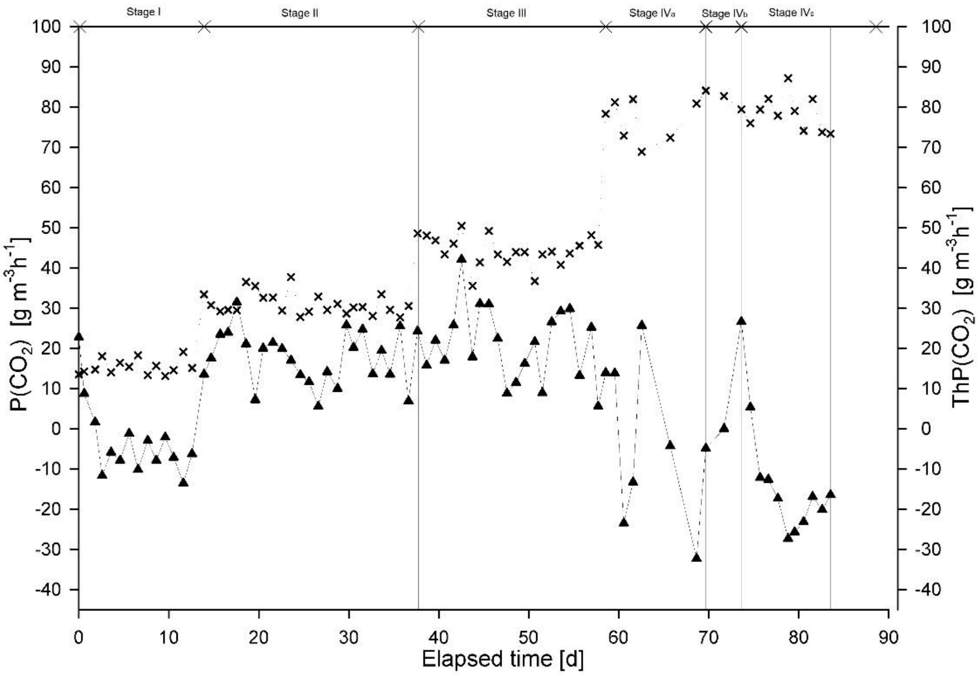


Figure 8-17: Time course of the real CO_2 production (PCO_2 —▲—) and the theoretical CO_2 production ($ThPCO_2$ ···×···) in the photobioreactor.

Indeed, a significant fraction of the CO_2 produced during pollutant mineralization in algal-bacterial systems is fixed by microalgae, resulting in a net CO_2 consumption.

Moreover, algal photosynthesis also ensured a high DO concentration in the cultivation medium (Rubio et al., 1999), which averaged 7.73 ± 0.94 mgO_2 L^{-1} throughout the experimental period. A mass transfer test was performed by increasing the toluene IL up to 11.13 ± 0.68 g $m^{-3}h^{-1}$ (Figure 8-12).

The increase in EC up to 9.93 ± 0.62 g $m^{-3}h^{-1}$ confirmed that toluene removal performance was limited by gas-liquid mass transfer. In stage II, the IL entering the TPBR was doubled to 9.29 ± 0.81 g $m^{-3}h^{-1}$, which resulted in an average RE of 87 ± 5% and an EC of 8.07 ± 0.77 g $m^{-3}h^{-1}$. CO_2 production rates increased concomitantly with the increase in toluene EC. Thus, a PCO_2 value of 17.56 ± 6.72 g m^{-3} h^{-1} (corresponding to almost half of the $ThPCO_2$) was observed (Figure 8-17).

The increase in IL mediated a higher O_2 consumption, which induced a slight decrease in the DO concentration of the cultivation broth compared with the previous stage (7.18 ± 0.56 mg L^{-1}).

The mass transfer test carried out in stage II revealed that toluene mass transport from the gas to the liquid phase was the limiting step at an EBRT of 1 min (Figure

8-13). A further increase in the IL during stage III (14.48 ± 0.77 g $m^{-3}h^{-1}$) lead to an increase in the EC up to 12.79 ± 3.08 g $m^{-3}h^{-1}$ (Figure 8-9).

A stable toluene removal was also recorded in this stage (RE = 89 ± 3%), where CO_2 production remained lower than the theoretical value (PCO_2 = 18.77 ± 12.53 g $m^{-3}h^{-1}$ *vs.* $ThPCO_2$ = 48.46 ± 11.82 g $m^{-3}h^{-1}$). No significant variations in the pH or the TSS concentrations were observed during stages II and III (average values of pH = 6.03 ± 0.8 and TSS = 119 ± 29 mg L^{-1}).

The mass transfer test in stage III confirmed process limitation by toluene mass transfer (*Figure 8-14*), since an increase in the IL of ×2.7 times (to 37.24 ± 2.35 g $m^{-3}h^{-1}$) resulted in an increase in the EC of ×2.6 (30.34 ± 3.06 g $m^{-3}h^{-1}$). Finally, when IL in stage IV was set at 23.42 ± 1.39 g $m^{-3}h^{-1}$, the TPBR supported an EC of 20.93± 1.50 g $m^{-3}h^{-1}$.

Interestingly, the increase in IL did not trigger a decrease in toluene RE, which remained stable at 89 ± 3%. It is worth noting that a higher biomass production was however recorded during stage IV, resulting in an increase in the algal biomass concentration (measured as TSS) from 170 to 410 mg L^{-1} from day 58 to 90.

The higher algal biomass concentration promoted the reduction in the net PCO_2 because of the enhanced photosynthetic activity (S. Bordel et al., 2007). A progressive decrease in the pH of the TPBR cultivation broth was recorded from day 68 onwards.

Despite no detrimental effect on process performance had been observed, the light intensity was increased to 148.31 µmol m^{-2} s^{-1} in order to increase the pH of the cultivation mediated by photosynthetic CO_2 uptake (Stage IVc). The higher light intensity resulted in a trend reversal in the pH (Xu et al., 2009).

The mass transfer test carried out by the end of the experiment highlighted that the system was also limited by mass transfer under the conditions implemented during stage IV (*Figure 8-15*).

8.2.3 Robustness test

A robustness test was performed by the end of the experiment to evaluate the capacity of both bioreactors to cope with fluctuations in the IL) and the results were reported in the Figure 8-18.

To this end, the toluene-loaded air feeding system was stopped for 3 days, while maintaining the mineral medium recirculation. The TPBR recovered the removal capacity immediately after the restoration of the polluted air supply, achieving a RE of 93 ± 3%.

On the contrary, the BTF did not achieve previous steady state removal efficiencies even after 46 hours from toluene feeding resumption. Indeed, a RE of 77 ± 5% was recorded nine hours after toluene feeding resumption, which was significantly lower than the removals recorded during stage IVc (86 ± 12%). Overall, the TPBR exhibited a higher process robustness towards process fluctuations than the BTF.

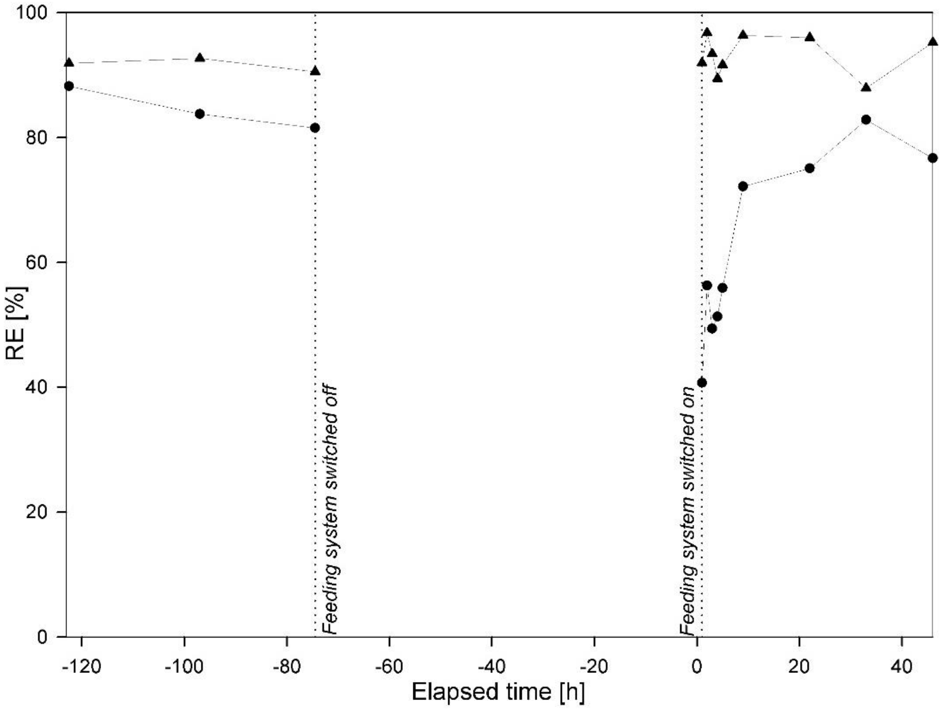


Figure 8-18: Time course of the RE in the BTF (—●—) and in the TPBR (—▲—) during the robustness test

8.2.4 Comparative evaluation

The initial RE of 30 % recorded in the TPBR following the start-up of both reactors was attributed to the higher absorption capacity of the photobioreactor cultivation broth (compared to the BTF that contained a significantly lower quantity of liquid medium).

During stage I, the bioreactors showed comparable performances with an EC higher than 3 g $m^{-3}h^{-1}$. However, the presence of the algal-bacterial consortium in the TPBR provided a synergic effect resulting in an increase in DO in the culture broth and the simultaneous CO_2 fixation.

For this reason, the TPBR rapidly showed CO_2 outlet concentrations significantly lower than those recorded in the BTF outlet. The BTF was also more sensitive towards the presence of secondary inhibitory metabolites due to the lower liquid volume and thus lower buffer capacity, their accumulation significantly affecting process performance during stage II. I

Indeed, the build-up of metabolites may trigger process instability due to their mutagenic effects on the culture (Leddy et al., 1995).

As previously observed by Bordel et al. (2007), the generation of secondary metabolites can be induced by a toluene overload, either as a result of an increase in the inlet concentration of toluene or a limiting O_2 concentration in the aqueous phase. In this context, the TPBR exhibited a higher adaptability to inlet load fluctuations both because of the larger amount of liquid involved (and therefore a significantly higher dilution) and of the higher DO concentrations in the cultivation broth. CO_2 consumption by microalgae also enhanced process stability by reducing the acidification effects resulting from toluene biodegradation.

Finally, the mass transfer tests pointed out that, regardless of the operational conditions, both processes were limited by toluene mass transfer from the gas phase to the biofilm or to the liquid phase.

It is important to highlight that during these mass transfer tests the PCO_2 remained stable, suggesting that pollutants accumulation did not occur and thus the toluene supplied to the bioreactors was mineralized by the microbial community.

However, when increasing the toluene inlet concentration, the TPBR supported an EC closer to the transient IL, which confirmed that the tubular photobioreactor responded better to higher toluene loads compared to the BTF.

8.2.5 Microbial community analysis

Read numbers after quality filtering and chimera filtering ranged between 77,059 (TPBR_0_MIX) and 34,891 (BTF_IV) (Table 8-1).

The number of resulting OTUs varied between 874 (BTF_0_AS) and 101 (BTF_IV) (Table 8-1). The inoculum of the BTF showed significantly higher OTU number and H and ID index values than the biofilm sample retrieved in the BTF by the end of the experiment (BTF_IV).

In this context, the simplification of the feed and the operating conditions applied mediated the reduction in the diversity of the microbial community in terms of species richness and evenness.

Accordingly, the number of phyla detected in BTF_0 was 34, decreasing to 14 in BTF_IV. Interestingly, the OTU number and H and ID indexes corresponding to the inoculum of the TPBR (a mixture of activated sludge and a microalgae-bacteria culture from a HRAP) were lower than those measured in the BTF_0_AS. This reduction was attributed to the enrichment of the most abundant species after the mixture (i.e. *Proteobacteria*) while the representation of the less abundant species decreased and could not be detected.

The operating conditions tested in the TPBR from stage II onwards resulted in a decrease in OTU richness compared to the inoculum, however H and ID indexes remained similar or even higher (i.e. TPBR_II), suggesting a more evenly distributed microbial community of most predominant groups.

From these data, it can be inferred that operating conditions mainly impacted the ID index, which mostly depends on the most abundant species, rather than the H index, which gives greater relevance to less abundant species.

Therefore, the specialization of the microbial communities to toluene feeding was mainly associated to a richness loss in the TPBR rather than to an evenness loss, which may have also contributed to an enhanced process stability in the TPBR (Haig et al., 2015; Wittebolle et al., 2009).

Table 8-1 OTU richness and Shannon and Inverse Simpson diversity indices during the different operational stages in the BTF and the TPBR.

Sample ID	**Non chimeric reads**	**OTUs (richness)**	**Shannon index**	**Inv. Simpson index**
BTF_0_AS	69,77	874	2,16	5,46
BTF_IV	34,89	101	1,08	2,38
TPBR_0_HRAP	57,45	276	1,50	2,89
TPBR_0_MIX	77,06	582	1,66	3,30
TPBR_II	52,02	171	1,85	5,68
TPBR_III	70,41	174	1,39	2,92
TPBR_IV	59,26	104	1,36	3,01

Proteobacteria was the most abundant phylum during the operation of the reactors (BTF_IV: 55 %, TPBR_III: 52 %, TPBR_IV: 49 %), except in TPBR_II, which was dominated by a wider range of bacterial phyla (*Proteobacteria*: 20 %, *Cyanobacteria*: 20 %, *Actinobacteria*: 18 %, *Bacteroidetes*: 18 %, *Chlamydiae*: 17 %) (Figure 8-19a).

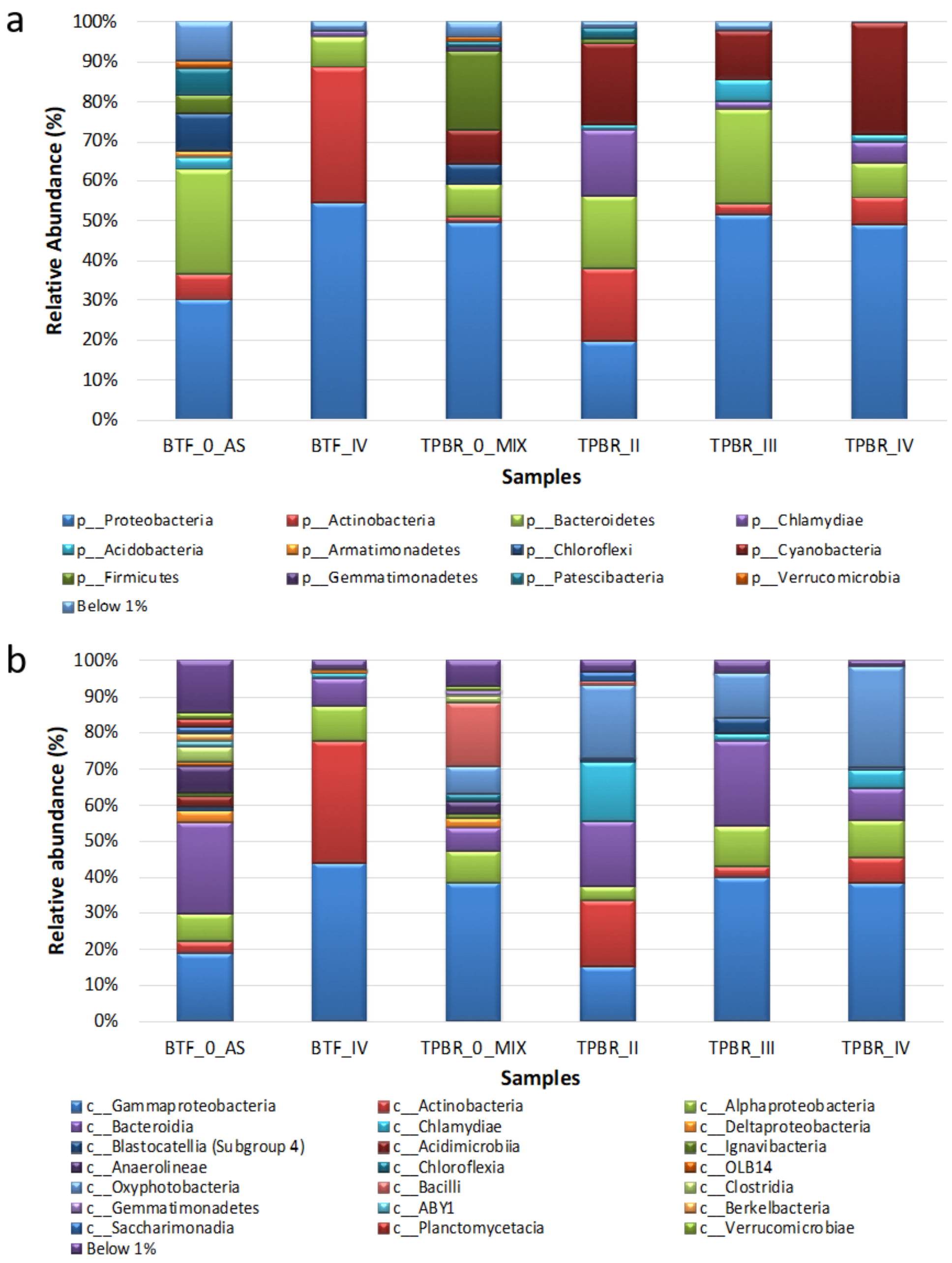


Figure 8-19: Bacterial community composition of the inocula, BTF and TPBR at the phylum (a) and class (b) taxonomic ranks.

Interestingly, *Actinobacteria* was more abundant in TPBR_II and BTF_IV samples, suggesting that toluene inlet concentration and the presence of photosynthetic organisms influenced its occurrence in the reactors.

This finding agreed with previous studies that identified *Proteobacteria* as the dominant group in an algal-bacterial airlift photobioreactor and bacterial reactor treating toluene at high inlet loads (369-480 g m^{-3} h^{-1}) (Estrada et al., 2012; Lebrero et al., 2016b).

At lower toluene loads (0.5 - 14 g m^{-3} h^{-1}), *Actinobacteria* (mostly *Mycobacterium* and *Pseudonocardia*) were mostly represented (Estrada et al., 2012). In this work, *Mycobacterium* and *Rhodococcus* were dominant, both genera being able to grow at low toluene concentrations (Juteau et al., 1999) (Figure 8-20).

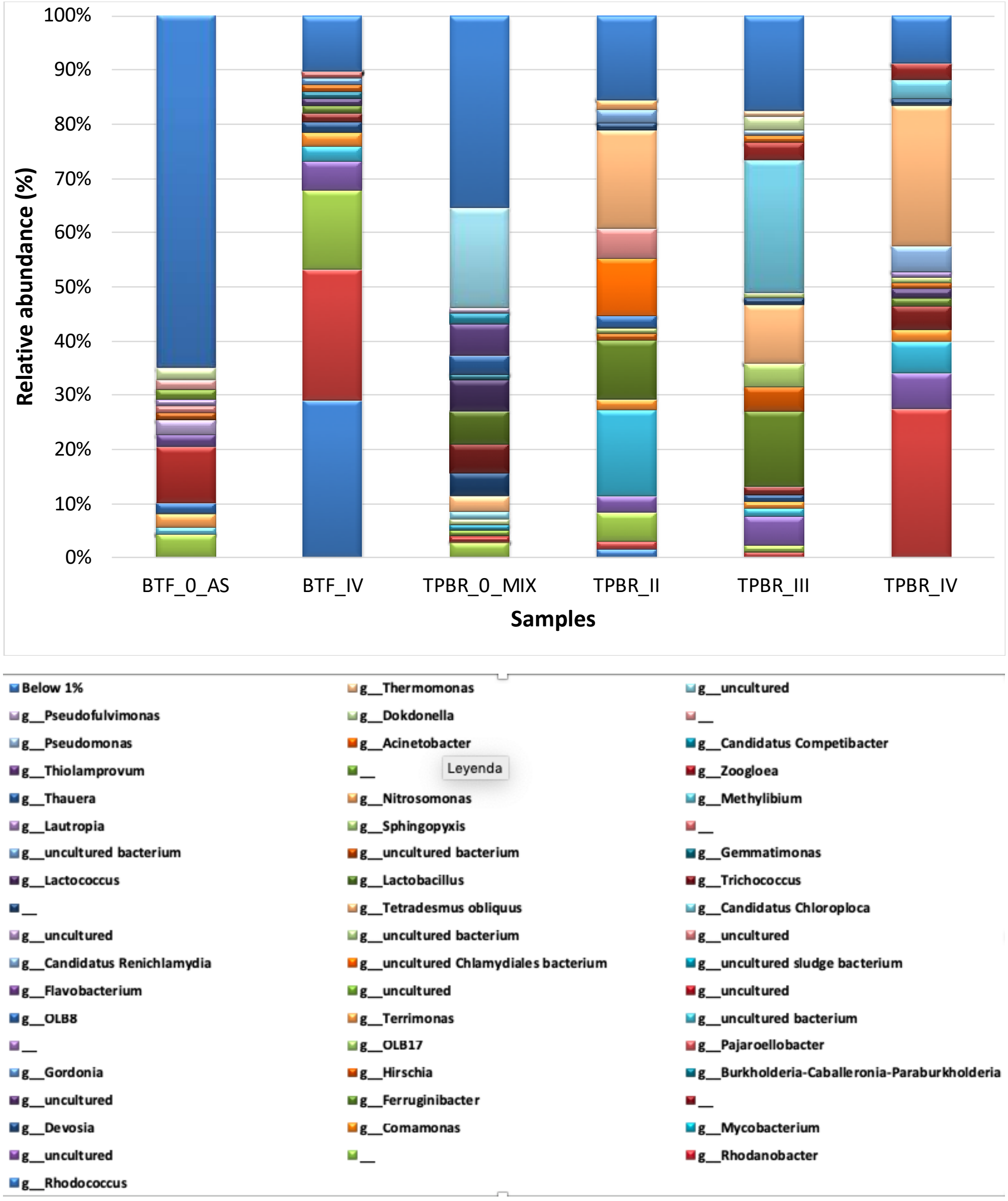


Figure 8-20: Bacterial community composition of the inocula, the BTF and the TPBR at the genus taxonomic rank

Among *Proteobacteria*, *Gammaproteobacteria* was a highly abundant class in all samples (Figure 8-19b). This class now includes *Betaproteobacteria* class as an order: the *Betaproteobacteriales* (Parks et al., 2018), which is a highly abundant group in rhizospheric and freshwater environments (Lünsmann et al., 2016a;

Martínez-Lavanchy et al., 2015; Zwart et al., 2002), where they play important roles in nitrogen cycling (Chen et al., 2003) and are known to produce plant growth promoting substances such as phytohormones (Sessitsch et al., 2005). *Betaproteobacteriales* (*Burkholderiaceae*) and *Xanthomonadales* (*Rhodanobacteraceae*) were dominant among *Gammaproteobacteria* (
Figure 8-21).

At the highest inlet load (stage IV), *Xanthomonadales* prevailed over *Betaproteobacteriales* in both the BTF and the TPBR (
Figure *8-21*a), highlighting their role at higher toluene concentrations. *Burkholderiales* have been identified as main toluene degraders (20 % of the entire bacterial community) in a constructed wetland; while most of the remaining bacterial community likely utilized other carbon sources derived from plant roots (Lünsmann et al., 2016a).

Similarly, bacteria in microalgal-bacterial consortium might utilize organic carbon released by microalgae, and in return, supply inorganic and low molecular weight organic carbon for algal growth, enhancing process stability in the TPBR (Cho et al., 2015).

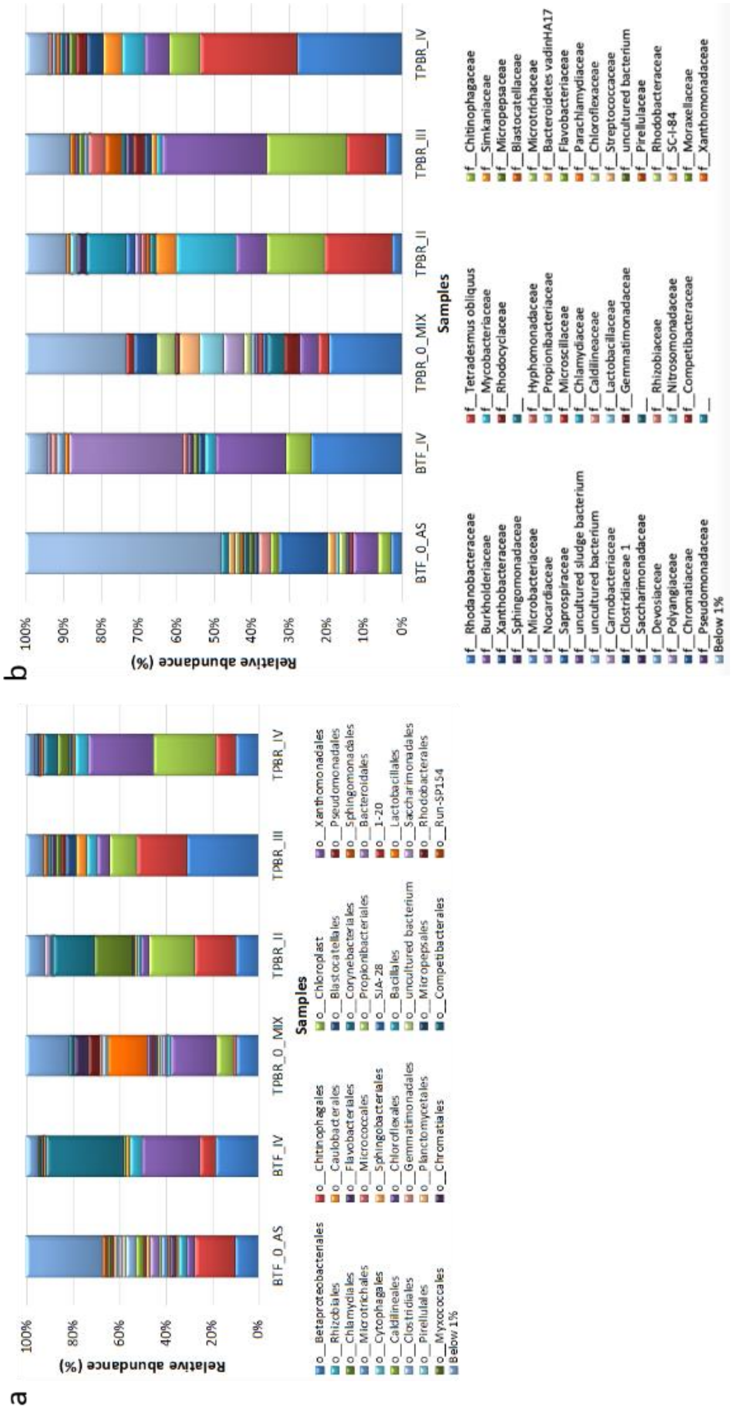


Figure 8-21: Bacterial community composition in the inocula, BTF and TPBR at the order (a) and family (b) taxonomic ranks.

In fact, it has been observed that *Burkholderiales* maintained stable toluene turnover in a constructed wetland treating toluene by feeding on organic root exudates, while reutilizing the stored carbon compounds (Lünsmann et al., 2016b). Many bacterial groups detected in the are able to grow in mutualistic association with several species of green algae (Krohn-Molt et al., 2017; Sambles et al., 2017) or even rely on an eukaryotic host for cell survival (Taylor-Brown et al., 2015) as is the case of *Chlamydiae* (Figure 8-19a).

This highlights the importance to unravel microalgae and bacteria interactions in algal-based photobioreactors to boost VOCs removal performance.

8.2.6 Microalgae population

Chlorella vulgaris and Chlorella minutissima were the dominant species in the inoculum of the TPBR (56 and 26 %, respectively) (Figure 8-22).

These species were gradually replaced by *Scenedesmus obliquus*, which was the dominant species (43 %) during stage II together with *Chlorella vulgaris* (29 %), *Chlamydomonas altera* (14%) and *Scenedesmus acuminatus* (14%). From this stage on, a gradual increase in the abundance of *Chlamydomonas sp*. was observed, which become the dominant species during stages III (48 %) and IV (63 %).

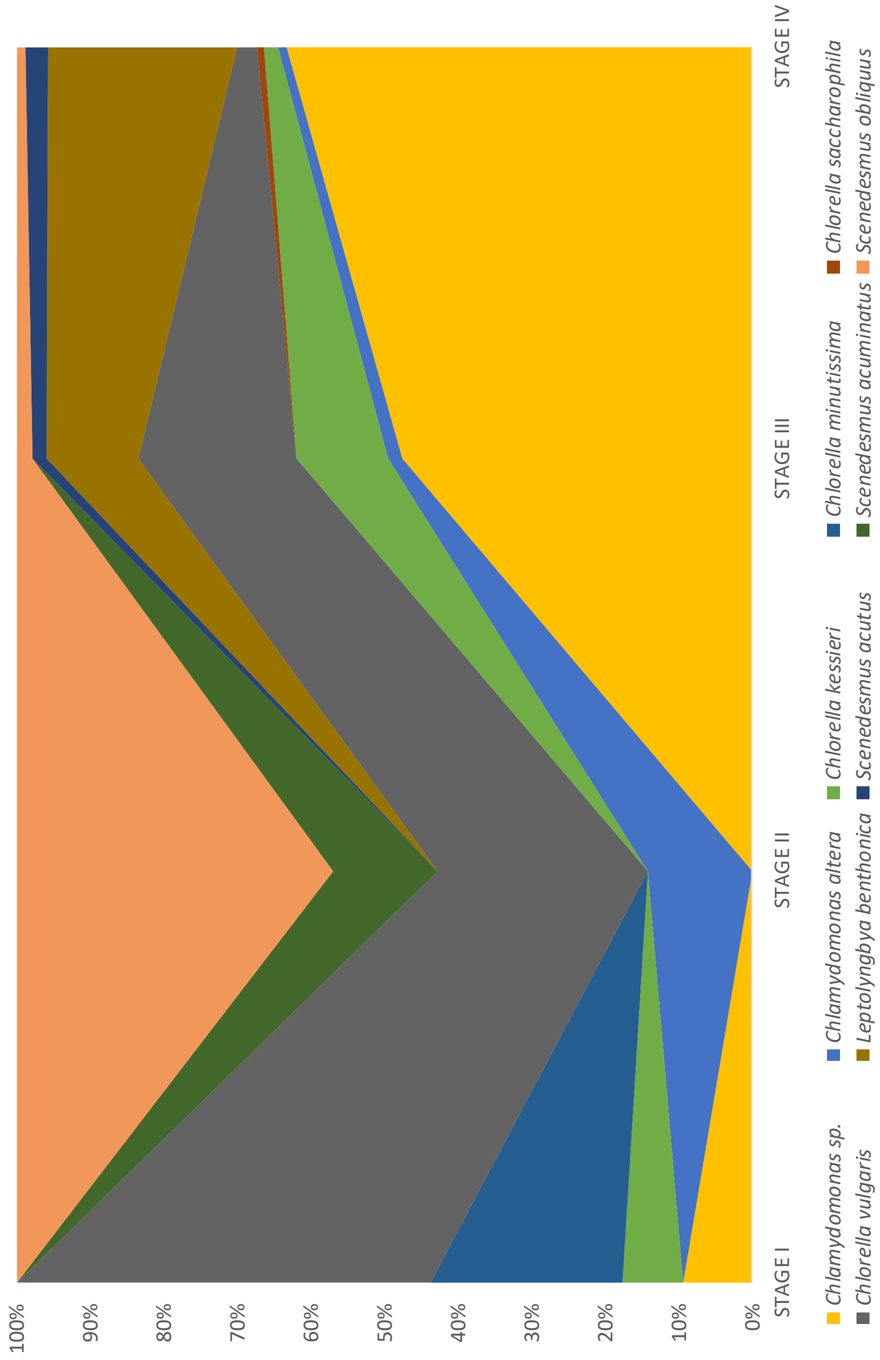


Figure 8-22: Evolution of the structure of the microalgae population in the TPBR

These genera are included among the top 8 genera of microalgae tolerant to organic pollution (Palmer, 1969).

Unfortunately, no specific correlation between operating conditions and the evolution of the microalgae population was elucidated.

Nevertheless, the evolution of the microalgae population was likely linked to the evolution of the bacterial communities, since it has been demonstrated that specific microalgae populations are associated with unique and specific microbial groups (Krohn-Molt et al., 2017).

9. Conclusions and future perspectives

In the last decades, has become always more clear the intrinsically connection between air pollution and human health.

Consequently, even if in the past it was attributed to atmospheric pollution a secondary importance in the attention paid for environmental protection issues, nowadays the increasing citizens awareness and the presence of several strict Regulations have boosted a great attention about these aspects in the technical and scientific communities.

Health effects, including mortality and morbidity owing to cardiovascular and respiratory diseases, have been indeed closely associated with the air pollutants concentrations (Hoek et al., 2013).

Odorous compounds and volatile organic compounds are typical outdoor air pollutants, with several adverse effects on health as well as on the social and physical environment (Balasubramanian et al., 2012).

Along with their smell offensiveness, VOCs and odorous gases even result in acute and chronic long-term health effects (Kim et al., 2011; Zhang and Tay, 2015).

In recent years, to improve air quality by reducing air pollution related to VOCs and odorous gases, various technologies have been investigated.

The conventional waste gas treatment technologies may be grouped in physical-chemical technologies and biological technologies.

The effective application of physical–chemical methods is achieved for the treatment of stream with contaminants concentration relatively high, since otherwise they could not be economically feasible.

Moreover, these technologies promote the transfer of gaseous pollutants to liquid or solid phases, with the move of the contamination without any effect of degradation.

AOPs processes are instead capable of promoting contaminants mineralization thanks to due action of the strong oxidants generated. However, the real-scale application of these technologies is still limited by operational problems related to the potential emission of toxic by-products and the high energy consumption.

For this reason, the application of AOPs as pre-treatment at conventional waste gas treatment technologies may be of key interest with a view at boosting removal performances besides the control of the by-products release and the energy required.

Gas phase toluene degradation by UV irradiation/ozonation was investigated and compared with the process upgraded with an additional step of scrubbing.

The increase in inlet toluene concentration led to the drop of the removal efficiency for the single-stage process. The main mechanism of the process was through the oxidation of toluene by hydroxyl radicals.

The additional water scrubbing phase facilitated further degradation of toluene and increased the ozone consumption.

The UV/O_3 process supported an effective toluene removal for inlet concentration less than 200 ppm, at the minimum applied voltage. For greater concentrations, higher voltage is needed to achieve adequate removal. At all investigated toluene concentrations, the removal efficiency increased as the applied voltage and, therefore, the ozone supplied to the system increased.

The combined process allowed the achievement of higher removal efficiencies. For inlet concentrations of 100 - 150 ppm the removal resulted higher than 95%, even at the minimum ozone dose applied. In the integrated UV/O_3+S process, the elimination capacity with the minimum applied voltage resulted for all the investigated conditions higher than the elimination of UV/O_3 process applying the maximum voltage.

The residual ozone resulting from UV/O_3 treatment may be easily used for the further degradation of the compounds not completely oxidized in the first phase of the process, since the high solubility in water of the oxidation by-products, ozone included.

In that view, the additional wet scrubbing step supported a more sustainable toluene degradation, both from an environmental and economic point of view, since it may be possible not only to significantly improve the performances of the process, valorising the high oxidizing capacity of the hydroxyl radicals released in water, but also to reduce the emission of gaseous by-products into the atmosphere.

Although the results observed suggest the feasibility of the application of AOPs as pretreatment at conventional processes, further studies should be focused on:

- the application of UV/O_3+S systems for the removal of VOCs mixtures, which may result in synergic or antagonistic effects among the different gaseous compounds and, consequently, in different process performances;
- evaluation of the applicability of UV/O_3 as pretreatment at a conventional bioscrubber, for the enhancement of compounds bio-treatability and the control of biomass accumulation (Covarrubias-García et al., 2017; Oller et al., 2011);
- detailed analysis in terms of costs and energy balance of the combined system at pilot scale;

- scale up of the combined system and its application at an industrial scale.

On the other hand, biotechnologies are currently recognized as the best available option for the treatment of low and moderate concentrated waste gases containing odorous pollutants and VOCs. Biological process allow to achieve good performances besides cost-effective and environment-friendly operation when compared with other physical and chemical technologies (Ryu et al., 2011).

It has been found that these technologies are able to treat diluted off-gases, with concentrations of VOCs typically lower than 3 g m^{-3}, with reduction yields for some pollutants up to 99% (Groenestijn and Kraakman, 2005).

In particular, BTF is recognised to have advantages over the biological competitors mainly consisting of lower pressure drop during long-term operation, lower sensitivity to the presence of acidic degradation products when high inlet loads are involved.

In this context, the present work also demonstrated the potential of the synergisms between bacteria and microalgae to support an effective and environmentally friendly toluene biodegradation.

The high DO concentrations and higher pH values mediated by photosynthesis resulted in improved and more stable performances in the TPBR compared to the BTF.

In this regard, average ECs of 13,58 ± 0,56 g $m^{-3}h^{-1}$ and REs of 88% ± 10% were achieved in the tubular photo-bioreactor. Consistently, several bacteria that grow in mutualistic association with green algae were detected in the TPBR.

The BTF (dominated by Proteobacteria and Actinobacteria at the end of the experiment) supported similar toluene removal, but it suffered from performance deterioration mainly due to secondary metabolites accumulation and acidification of the recirculating medium, which inhibited microbial activity.

Moreover, CO_2 fixation by microalgae in the TPBR resulted in a reduction in CO_2 emissions and the production of a valuable biomass suitable for further revalorization.

Despite the satisfactory performance of both systems, the photobioreactor presented a competitive advantage due to the capacity of algal biomass to fix the produced CO_2, considerably reducing the emissions of this greenhouse gas, while increasing the concentration of dissolved oxygen in the cultivation broth up to 7.7 mg O_2 L^{-1}.

The benefits derived from the application of this solution may be attributed to the increasing in DO cultivation in culture growth and the increase in toluene biotreatability thanks to microalgae activity.

Thus, the results obtained in the present study confirmed the suitability of this innovative TPBR set up to efficiently treat toluene emissions while reducing the carbon footprint of the conventional biological technologies.

Overall, the synergism between microalgae and bacteria may be considered an effective solution for the simultaneous abetment of greenhouse gases and toluene.

Although the results observed suggest the feasibility of the application of TPBR for the simultaneous abetment of greenhouse gases and VOCs, further studies should be focused on:

- the application of TPBR for the removal of VOCs mixtures, which may result in synergic or antagonistic effects among the different gaseous compounds and, consequently, in different process performances;
- detailed analysis in terms of costs and energy balance of the proposed system at pilot scale;
- evaluation and quantification of the materials and energy recovery from algal biomass produced in TPBR;
- scale up of the system and its application at an industrial scale.

Based on the evidences resulting from this work, it should be stated that when low inlet concentrations are expected, biotechnologies could be considered the best options since these kind of processes resulted able to achieve high REs, besides low environmental and economic impacts (Muñoz et al., 2015, Oliva et al., 2018).

Conversely, when high capacity performances are required, AOPs may be considered a more effective solution.

In particular, hybrid process could be implemented, with a view at promoting an Advanced Oxidation pre-treatment, reducing the energy consumption of a single stage AOPs followed by a wet scrubbing process, for the reduction of by-product release.

The combination of conventional and advanced oxidation processes could be considered hence a sustainable platform to reduce the emission of undesirable by-products, besides treating high concentrations of VOCs (Oliva et al., 2018; Angèles et al., 2018).

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