INDOOR AIR TREATMENT BY COUPLING BIOFILTRATION & ADSORPTION

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Doctoral thesis under joint-supervision

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Acronyms

UPV	Universidad del Pais Vasco
UPPA	Université de Pau et des Pays de l'Adour
MEB	Microscope à balayage électronique
IAQ	Indoor air quality
VOC	Volatile organic compounds
IAP	Indoor air pollution
UV	Ultraviolet radiation
EBRT	Empty bed residence time
RE	Removal efficiency
WHO	World health organization
BTEX	Benzene, toluene, ethylbenzene and xylenes
TEX	Toluene, ethylbenzene and xylenes
IQMA	Departamento de Ingenieria Quimica y del Medio Ambiente de la UPV
LaTEP	Laboratoire de Thermique, energétique et procédés
SBS	Sick building syndrome
BRI	Building related illness
MCS	Multiple chemical sensitivity
ANSES	French Agency for Food, Environmental and Occupational Health & Safety
USA	Unite States of America
PAH	Polycyclic aromatic hydrocarbons
TVOC	Total Volatile Organic Compounds
PM	Particulate matter
EC	Elimination capacity
EPA	Environmental Protection Agency
US	United States
EMF	Electromagnetic fields
OSHA	American Occupational Safety and Health Administration
HEPA	High Efficiency Particle Arresting
NTP	Non-thermal plasma
CADR	Clean air delivery rate
RH	Relative humidity
IPC	In-plasma catalysis
PPC	Post- plasma catalysis
PCO	Photocatalytic oxidation
BTF	Biotrickling filter
MBR	Membrane bioreactor
PVC	Polyvinyl-chloride

EU	European union
OQAI	Observatory of Indoor Air Quality
BF	Biofiltration
HS	Hybrid system
CNS	Central nervous system
NIOSH	American National Institute for Occupational Safety and Health
PEL	Permissible exposure limit
IDLH	Immediately dangerous to life or health
VTR	Reference toxicological value
STEL	Short term exposure level limit
IL	Inlet load
EC	Elimination capacity
AC	Activated carbon
SEM	Scanner electron micrographs
ASTM	ASTM International standards
DM	Mass flowmeter
FID	Flamme ionization detector
MS	Mass spectrometer
NIST	US National Institute of Standards and Technology
GC	Gas chromatography
ELPI	Electrical Low Pressure Impactor
BET	Brunauer–Emmett–Teller theory
CFU	Colony forming units
PUF	Polyurethane foam
CEC	Cation-exchange capacity
COD	Chemical oxygen demand
TOC	Total organic carbon
WWTP	Wastewater treatment plant
DGGE	Denaturing Gradient Gel Electrophoresis
NMHC	Non-methane hydrocarbons

Abstract

Indoor air quality (IAQ) plays an important role in people's health and well-being because population spends a substantial fraction of their life within indoor places. Indoor pollutant concentrations have risen to hazardous levels not only as a result of new consumer patterns but also, under the influence of energy efficiency policies in buildings. The volatile organic compounds (VOC) are the major contributors to the deterioration of IAQ. These compounds are emitted from a wide range of sources including building materials and human activities (i.e. cooking, cleaning and gardening), and can be generated as secondary pollutants from indoor gas-phase reactions. Likewise, the transfer from the outdoor environment significantly contributes to the indoor air pollution (IAP).

Nowadays, the treatment of IAP is carried out by the use of air cleaning technologies that involve principally media filtration, adsorption, photocatalytic oxidation, plasma technology and UV photolysis. Nevertheless these devices have been judged for their high energy consumption and the generation of by-products. Accordingly, there is currently no technology that can be considered fully satisfactory for achieving "cleaner" indoor air.

In the present thesis, a general introduction to the work carried out within the context of this thesis is presented in chapter 1. In chapter 2, the scope and extend of the thesis is presented.

An overview of indoor air pollution and the purification technologies that treat it are presented in chapter 3. Special attention is given to combined technologies as these systems seem to be the best option to treat the variety of indoor pollutants because they integrate synergetic advantages of different processes. Although further studies of the performance of combined technologies in real indoor environments are necessary before their deployment in confined spaces.

Recently, biotechnologies such as biofiltration and botanical purification have emerged as attractive alternatives to control air pollution. In fact, biofiltration is easy to implement, involves a destructive process, has high removal efficiency for a large range of chemical compounds and is cost-effective and environmentally friendly. Nevertheless, biofiltration is very sensitive to load fluctuations, does not treat non-biodegradable compounds, might emit bio-by-products and requires a large area for its installation. These limitations could be overcome by coupling this technique with other processes such as adsorption technology which offers a good response in the case of load fluctuations, can treat several indoor contaminants and does not have significant space requirements. Those techniques were used in the study presented in chapter 4.

The overall objective of chapter 4 was to compare biofiltration technology and the hybrid system-biofiltration-adsorption (onto activated carbon) as possible methods to treat indoor air pollution. A mixture of toluene and p-xylene was chosen as characteristic indoor pollutants for this study. An organic material was used as packing material for the biofiltration stage considering its good performance in similar studies conducted by the Biofiltration Research Group at the Engineering Faculty in Bilbao (University of the Basque Country, UPV/EHU). The acclimation of this material was carried out for 100 days for the mixture of toluene and p-xylene removal at concentration ranges of 65-275 ppm and 19-89 ppm, respectively. These concentrations were higher than those normally found in indoor environments (ppb or µg m^{-3}) but they could represent concentration peaks associated with specific indoor activities such as cooking and cleaning or concentrations in specific places such as bus stations and underground car parks. The Empty Bed Residence Times (EBRTs) used in this study were 120 s and180 s. At the highest time, the toluene removal efficiency reached values >80 % at the end of the experimental time but only a maximum removal efficiency of 45 % was recorded for the p-xylene.

Since the EBRT is an essential parameter in biofilters' design, chapter 4 also presents a specific study during 60 days considering low EBRTs (6-12 s) in the operation of a biofilter packed with compost and treating toluene and p-xylene at average concentrations of 288 and 213 ppb, respectively. Even at these low EBRTs and concentrations, toluene removal efficiency reached 100% at day 35 and p-xylene showed an increasing trend in their removal efficiency (RE) over the time with a maximum of 65%.

Additionally, in chapter 4, the assessment of by-products and particles generation by the biofilter and the hybrid systems was taken into account. This aspect is one of the main highlights of this study considering that most of the researches in indoor air treatments are predominantly focused on the contaminants removal and less on their secondary impacts. Acetone and acetic acid were identified as by-products of the biofilter. Particle emissions in the range of 0.03 to 10 µm (particle diameter) were recorded for both systems which suggest the necessity of using a particle filter at the end of the process chain.

Another specificity of indoor air pollution that could limit the use of biofiltration in close environments is the presence of concentration peaks associated to specific indoor activities. chapter 5 focuses on the assessment of the hybrid system efficiency (biofiltration-adsorption) in the treatment of toluene at concentrations close to those found in real indoor air environments but also when concentration peaks were generated for a few hours per day. Biofiltration showed a good removal efficiency at low pollutant concentrations, but was sensitive to rapid changes in inlet loads (concentration peaks) even at very low toluene concentrations. The adsorption column placed downstream of the biofilter was however able to deal with those concentration peaks and thus, to maintain a high overall efficiency of the hybrid system. An approach of the design of the system was also presented in this section.

In Chapter 6, special confined environments with high concentration levels due to vehicular traffic are also considered. The feasibility of re-using two soils recovered from construction sites as the media in a biological system for the treatment of this pollution was assessed.

These soils were completely characterized and used each one in two lab-scale biofilters to treat a mixture of toluene, ethylbenzene and p-xylene, chosen as representative contaminants generated by vehicular combustion engines. There are no previous publications in which the possibility of simultaneously treating these compounds with soil generated by construction sites was analysed. Biofilters resilience was studied under progressive increases in pollutant loading and operational alternate periods and one soil stood out to be more suitable for biofiltration process.

In brief, biofiltration is able to achieve high removal efficiencies for the target pollutants at low EBRTs and concentrations. Nevertheless, ahead of the heterogeneity of indoor pollutants, operational disruptions and generation of by-products, the hybrid system was the most robust and turned out to be the best alternative in the treatment of indoor air pollution according to the operating conditions herein tested.

Resumen

La calidad del aire interior juega un papel importante en la salud de las personas y su bienestar puesto que la población pasa una parte importante de su vida dentro de lugares cerrados. Las concentraciones de contaminantes en el interior han aumentado a niveles peligrosos, no sólo como consecuencia de los nuevos patrones de consumo, sino también, bajo la influencia de las políticas de eficiencia energética en las habitaciones. Los compuestos orgánicos volátiles (COV) son los principales contribuyentes del deterioro de la calidad del aire interior. Estos compuestos son emitidos desde una amplia gama de fuentes, incluyendo los materiales de construcción y las actividades humanas como la cocina, la limpieza y jardinería, entre otras. También pueden ser generados como contaminantes secundarios de reacciones en fase gaseosa en el interior. Del mismo modo, el traslado de agentes contaminantes desde el exterior de las habitaciones a zonas interiores contribuye significativamente a la contaminación del aire interior (CAI).

Hoy en día, el tratamiento de la CAI se lleva a cabo mediante el uso de tecnologías que implican principalmente la filtración, la adsorción, la oxidación fotocatalítica, la tecnología de plasma y la fotolisis UV. Sin embargo, estos dispositivos han sido juzgados por su alto consumo de energía y la generación de subproductos. En consecuencia, no existe actualmente ninguna tecnología que pueda considerarse plenamente satisfactoria en la generación de un aire interior más limpio.

En el primer capítulo de la presente tesis aparece la introducción general al trabajo efectuado en el marco de este proyecto de co-tutela. El segundo capítulo presenta los objetivos de la tesis.

Una visión general de la contaminación del aire en interiores y las tecnologías de purificación que lo tratan son presentadas en el Capítulo 3. Especial atención se le da a las tecnologías combinadas ya que estos sistemas parecen ser la mejor opción para tratar la variedad de contaminantes interiores, al integrar las ventajas de los diferentes procesos. Sin embargo, otros estudios del rendimiento de las tecnologías combinadas en ambientes reales son necesarios antes de su implementación en espacios cerrados.

Recientemente, las biotecnologías como la biofiltración y la purificación botánica se han convertido en alternativas atractivas para el control de la contaminación del aire. De hecho, la biofiltración puede ser una buena alternativa para el tratamiento de la CAI, debido a que es fácil de implementar, implica un proceso destructivo, tiene una alta eficiencia de remoción para una gran variedad de compuestos químicos y es rentable y ecológica. Sin embargo, la biofiltración es sensible a las fluctuaciones de carga, no trata los compuestos no biodegradables y podría emitir bio-subproductos. Estas limitaciones podrían superarse mediante el acoplamiento de esta técnica con otros procesos tales como la tecnología de adsorción que ofrece una buena respuesta en el caso de fluctuaciones de carga, puede tratar

varios contaminantes y no requiere mucho espacio a la hora de implementarse en interiores. Estos dos procesos (biofiltación y absorción) se utilizaron en el estudio presentado en el Capítulo 4.

El objetivo general del Capítulo 4 fue comparar la tecnología de biofiltración y el sistema híbrido de biofiltración-adsorción como posibles métodos para el tratamiento de la contaminación del aire interior. El tolueno y el p-xileno fueron elegidos como contaminantes interiores característicos en este estudio. Un material orgánico suministrado por una empresa española se utilizó como soporte para la etapa biofiltración, teniendo en cuenta su buen desempeño en estudios similares llevados a cabo por el Grupo de Investigación en Biofiltración de la Facultad de Ingeniería de Bilbao (Universidad del País Vasco).

Considerando que el tiempo de residencia del gas (conocido como EBRT) es un parámetro esencial en el dimensionamiento de un biofiltro, el Capítulo 4 también presenta un estudio específico considerando bajos valores de EBRT (6-12 s) en la biofiltración de tolueno y p-xyleno a niveles de concentración de 147 y 87 ppb, respectivamente. Se demostró que incluso a bajas concentraciones ($\mu g\ m^{-3}$ o ppb) el proceso de biofiltración es capaz de lograr altas eficiencias en la eliminación de estos contaminantes a bajos EBRT.

Además, este estudio tuvo en cuenta la evaluación de la generación de subproductos y partículas, que es una de los principales atractivos de este estudio, teniendo en cuenta que la mayor parte de las investigaciones en tratamientos del aire interior son predominantemente centradas en la eliminación de contaminantes y menos en sus efectos secundarios.

Otra característica de la contaminación del aire interior que podría limitar el uso de la biofiltración en entornos cerrados, es la presencia de picos de concentración asociados a las actividades interiores específicas, como la cocina, la limpieza o la puesta en marcha de los vehículos en los parqueaderos interiores. El Capítulo 5 se centró en la evaluación de la eficiencia del sistema híbrido (biofiltración-adsorción) en el tratamiento de tolueno en concentraciones reales cercanas a las que se encuentran en ambientes interiores y también cuando se generan picos de concentración durante algunas horas por día. La biofiltración mostró una buena eficiencia de remoción a bajas concentraciones de contaminantes, pero fue sensible a los cambios rápidos en la carga de entrada (picos de concentración), incluso en concentraciones muy bajas de tolueno. La columna de adsorción colocada aguas abajo del biofiltro fue capaz de tratar los picos de concentración y, por tanto, mantener una alta eficiencia global del sistema híbrido.

En el Capítulo 6 se consideraron espacios confinados especiales con altos niveles de contaminantes asociados al tráfico vehicular. Se evaluó la viabilidad de la reutilización de dos suelos recuperados de obras de construcción como soportes de sistemas biológicos para el tratamiento de este tipo de contaminación. Estos suelos fueron completamente caracterizados y usados cada uno en dos biofiltros a escala de laboratorio para tratar tolueno, etilbenceno y p-xileno, elegidos como contaminantes representativos generados por vehículos. No hay

publicaciones anteriores en las que se haya analizado la posibilidad de tratar estos compuestos con suelo generado por las obras de construcción como medio de biofiltración. La resiliencia de los biofiltros se estudió con aumentos progresivos en la carga contaminante y períodos alternos operacionales; los suelos presentaron características adecuadas para el proceso de biofiltración.

En resumen, la biofiltración es capaz de lograr altas eficiencias de eliminación para los contaminantes a concentraciones bajas y EBRT bajos. Sin embargo, frente a la heterogeneidad de los contaminantes en aires interiores, las interrupciones operacionales y la generación de subproductos, el sistema híbrido fue el más robusto y resultó ser la mejor alternativa en el tratamiento de la contaminación del aire interior de acuerdo con las condiciones de operación probadas en los diferentes estudios llevados a cabo a lo largo del desarrollo de la presente tesis.

Résumé

La qualité de l'air intérieur (QAI) joue un rôle important dans les domaines de la santé et du bien-être des gens. La population humaine passe une part importante de son temps dans des endroits clos, dans lesquels les concentrations de polluants ont augmenté en raison de nouveaux modes de consommation mais également sous l'influence des politiques d'efficacité énergétique du bâtiment, pour atteindre aujourd’hui des niveaux dangereux pour la santé. Les composés organiques volatils (COV) sont les principaux contributeurs de la détérioration de la QAI. Ces composés sont émis par un large éventail de sources (certains matériaux de construction par exemple) où les activités humaines peuvent prendre une part importante (cuisson, nettoyage et jardinage). Le transfert de polluants à partir de l’environnement extérieur contribue de plus de manière significative à la pollution de l'air intérieur (PAI). Enfin, des polluants secondaires peuvent être générés par des réactions en phase gazeuse au sein de l’air intérieur.

Aujourd'hui, le traitement de la PAI est réalisé à partir de technologies impliquant principalement la filtration, l'adsorption, l'oxydation photocatalytique, le plasma et la photolyse UV. Néanmoins, certains de ces dispositifs ont une forte consommation d'énergie et/ou génèrent des sous-produits. En conséquence, il n'y a actuellement aucune technologie qui peut être considéré comme pleinement satisfaisante pour obtenir un air intérieur "propre".

Le premier chapitre est une introduction générale au travail effectué dans le cadre de cette thèse.

Le chapitre deux présente les objectifs de la thèse.

Dans cette thèse, un aperçu général de la pollution de l'air intérieur et des technologies de purification qui tentent de la traiter sont présentés au chapitre 3. Le couplage des procédés a reçu une attention particulière car seuls ces couplages, en intégrant les avantages synergiques de différentes technologies, semblent capables de traiter la grande variété des polluants que l’on trouve dans l’air intérieur. Mais beaucoup d'autres études sur le comportement et les performances de ces technologies combinées sont nécessaires, dans des environnements réels intérieurs, avant que leur déploiement dans des espaces confinés soit envisagé.

Récemment, les biotechnologies (biofiltration, purification botanique, etc.) ont émergé et peuvent constituer des moyens intéressants pour contrôler la pollution de l'air. La biofiltration est facile à mettre en œuvre ; c’est un procédé destructif qui a un rendement d’élimination élevé pour une large gamme de composés chimiques. Elle est en outre peu onéreuse et respectueuse de l'environnement. Par contre, c’est une technologie particulièrement sensible aux fluctuations de charges et qui ne traite pas les composés non biodégradables. Elle peut en outre émettre des sous-produits biologiques et elle mobilise une surface d’installation importante. Ces limitations peuvent être surmontées en couplant cette technique avec d'autres procédés, comme ceux utilisant l'adsorption, pour obtenir un dispositif qui peut traiter un

grand nombre de polluants et qui offre une bonne réponse dans le cas de fluctuations de charge tout en ayant peu d’exigences en ce qui concerne l’espace d’occupation. L’étude du couplage de la biofiltration et de l’adsorption est présentée dans le chapitre 4.

L'objectif global de ce chapitre est de comparer les performances d’un système de biofiltration et d’un système hybride biofiltration-adsorption (sur du charbon actif) pour traiter la pollution de l'air intérieur. Un mélange de toluène et de p-xylène a été choisi dans le cadre de cette étude car ces deux composés sont représentatifs de la pollution de l’air intérieur. En raison de ses bonnes performances, un compost déjà utilisé au cours d’études menées par le Groupe de recherche sur la biofiltration à la Faculté de Génie à Bilbao (Université du Pays Basque, UPV / EHU) a été utilisé comme media pour la partie biofiltration . L'acclimatation de ce média a été effectuée pendant 100 jours par un mélange toluène/p-xylène à des gammes de concentrations variant de 65 à 275 ppm et de 19-89 ppm, respectivement. Ces concentrations sont plus élevées que celles normalement rencontrées dans les environnements intérieurs (qui sont de l’ordre du $\mu g\ m^{-3}$ ou du ppb), mais elles peuvent être représentatives de pics de concentration associés aux activités intérieures spécifiques qui ont lieu dans les cuisines ou lors de périodes de nettoyage par exemple ; elles peuvent être également représentatives des concentrations que l’on trouve dans des endroits très spécifiques tels que les stations de bus ou les parkings souterrains. L’EBRT utilisée dans cette étude varie entre 120 s et 180 s. La valeur la plus élevée permet d’atteindre une efficacité d'élimination du toluène supérieure à 80% à la fin de la période expérimentale, alors qu’elle n’est que de 45% au maximum pour le p-xylène.

L’EBRT étant un paramètre essentiel dans la conception des biofiltres, le chapitre 4 présente également une étude spécifique qui s’étend sur une période de 60 jours et qui s’intéresse aux très faibles valeurs de cette grandeur (6-12 s). Un biofiltre utilisant du compost a été mis en place pour traiter du toluène et du p-xylène à des concentrations moyennes respectives de 147 ppb et 87 ppb. Même à ces faibles concentrations et pour ces faibles valeurs d’EBRTs, l'efficacité d'élimination du toluène a atteint 100% à partir du 35ème jour ; l’élimination maximale du p-xylène est de 65%, mais avec une efficacité qui augmente au cours du temps.

L'évaluation de la génération de sous-produits et de particules par le biofiltre et le système hybride a été prise en compte et est également présentée dans ce chapitre. Etant donné que la plupart des travaux de recherche concernant les traitements de l'air intérieur sont principalement axés sur l'élimination des polluants et moins sur leurs impacts secondaires, cet aspect est l'un des sujets saillants de cette étude. L'acétone et l'acide acétique ont été identifiés comme sous-produits de la biofiltration. Des émissions de particules dont le diamètre varie entre 0,03 µm à 10 µm ont été constatées pour les deux systèmes, ce qui suggère la nécessité de placer un filtre à particules en aval de la chaîne de procédés.

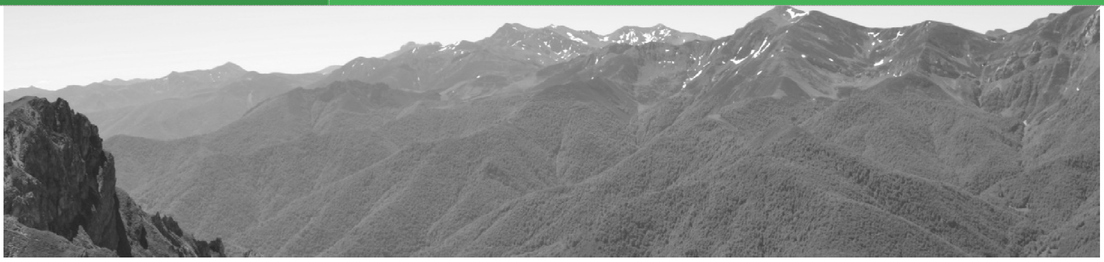
La présence de pics de pollution de l'air intérieur associés aux activités intérieures spécifiques peut limiter l'utilisation de la biofiltration dans des environnements clos. Le chapitre 5 est axé sur l'évaluation de l'efficacité du système hybride (biofiltration-adsorption) dans le traitement du toluène à des concentrations proches de celles trouvées dans l'air intérieur, mais également lors des pics de concentration de quelques heures par jour. La biofiltration est un procédé d'élimination très efficace des polluants à faibles concentrations, mais ses performances sont très sensibles aux changements rapides de charges polluantes en entrée (pics de concentration). La colonne d'adsorption placée en aval du biofiltre permet de traiter ces pics de pollution et donc de maintenir un haut rendement global du système hybride. Une première réflexion concernant la conception de ce système couplé est également présentée dans ce chapitre.

Finalement, certains environnements confinés particuliers, caractérisés par des concentrations très élevées de polluants issus de la circulation de véhicules ont été étudiés dans le chapitre 6. La réutilisation potentielle, comme médias de systèmes biologiques pour traiter cette pollution, de matériaux récupérés sur deux sols différents de chantiers de construction a été étudiée. Ces matériaux ont été caractérisés et utilisés chacun dans deux biofiltres à l'échelle du laboratoire pour traiter un mélange de toluène, d'éthylbenzène et de p-xylène, choisis comme polluants représentatifs générés par les moteurs à combustion internes de véhicules automobiles. A la connaissance de l'auteur, il n'y a pas de publications antérieures dans lesquelles la possibilité de traiter simultanément ces composés avec des matériaux issus de sols de chantiers de construction a été prise en compte. La résilience des biofiltres a été étudiée en faisant varier les concentrations de polluants et en établissant des périodes alternées de fonctionnement.

En conclusion, la biofiltration est capable d'atteindre de hauts rendements d'élimination pour les polluants cibles à faible EBRTs et à faibles concentrations. Néanmoins, face à l'hétérogénéité des polluants de l'air intérieur, des interruptions opérationnelles et de la génération de sous-produits, le système hybride biofiltration-adsorption est un dispositif robuste qui s'est avéré être une bonne alternative pour traiter la pollution de l'air intérieur.

CHAPTER 1

GENERAL INTRODUCTION



1. GENERAL INTRODUCTION

The World Health Organization (WHO) recently reported that in 2012, 4.3 million deaths were related to indoor air pollution and 3.6 million were attributable to ambient air pollution (WHO, 2014). In fact, pollution of indoor environments is often much higher than outdoors and is nowadays a public health issue (Geiss *et al.* 2011). It is estimated that indoor air quality (IAQ) determines, to a large extent, occupant health, comfort and productivity (WCB, 2005). Impacts resulting from poor IAQ include serious health issues (i.e. allergies, asthma, cancers, sick building syndrome, etc), which give rise to significant costs associated with health care expenses and work performance deterioration (Fisk, 2000; Mendell *et al.*, 2003). In this context, major efforts should be made to enhance IAQ. Three basic approaches are suggested to be applied in order to improve IAQ (Siegel, 2015).

The first strategy focuses on the control of the pollution source, which can be accomplished by its removal, confinement, or replacement (Liébana and Calleja 1998). This approach is often not possible because the indoor air is polluted by myriad of chemicals released from different sources such as construction materials, products and appliances (i.e. composite-wood, plasticizers, foam insulation, paints, cleaning agents, heaters, photocopiers and printers) (Weschler C.J., 2009). Daily indoor activities such as cooking, gardening and heating also release a great amount of chemical compounds.

Since sealed constructions and inappropriate ventilation rates in buildings are pointed out as responsible for the indoor air quality deterioration, the second strategy involves improving the ventilation system by increasing the amount of outdoor air to dilute indoor pollutant concentrations. Nevertheless, this alternative does not necessarily negate the presence of pollutants above a safe limit (Zaatari *et al.* 2014) and may involve the potential risk of simply bringing in more pollutants from the outside, and in addition, it is inconsistent with energy saving policies (Chithra and Shiva-Nagendra 2012). Finally, the third strategy involves the use of purification technologies. A review about this subject is presented in Chapter 3.

In the research environment, the number of articles published in relation to air cleaning technologies has increased in the last decade. Figure 1 shows publications related to indoor air treatments between the years 2002 and 2012 (research performed in SCOPUS). Filtration appears as the most studied air cleaning technology which concurs with the actual market that focuses on particle removal. Adsorption and photocatalysis have also been commercialized in the last decade but secondary impacts are derived from their use. Recently, biofiltration, plasma, botanical purification and membrane separation methods have emerged and seem to be promising technologies in indoor environments. Regarding ozonation, this might be excluded from the emerging methods because even if there are few publications on the matter, ozone generators were widely used until recent studies showed that they produce ozone concentrations that pass the limit set by the U.S. Food and Drug Administration (0.05 ppm by volume of air passing through the device) (Consumers Union of U.S., 2007).

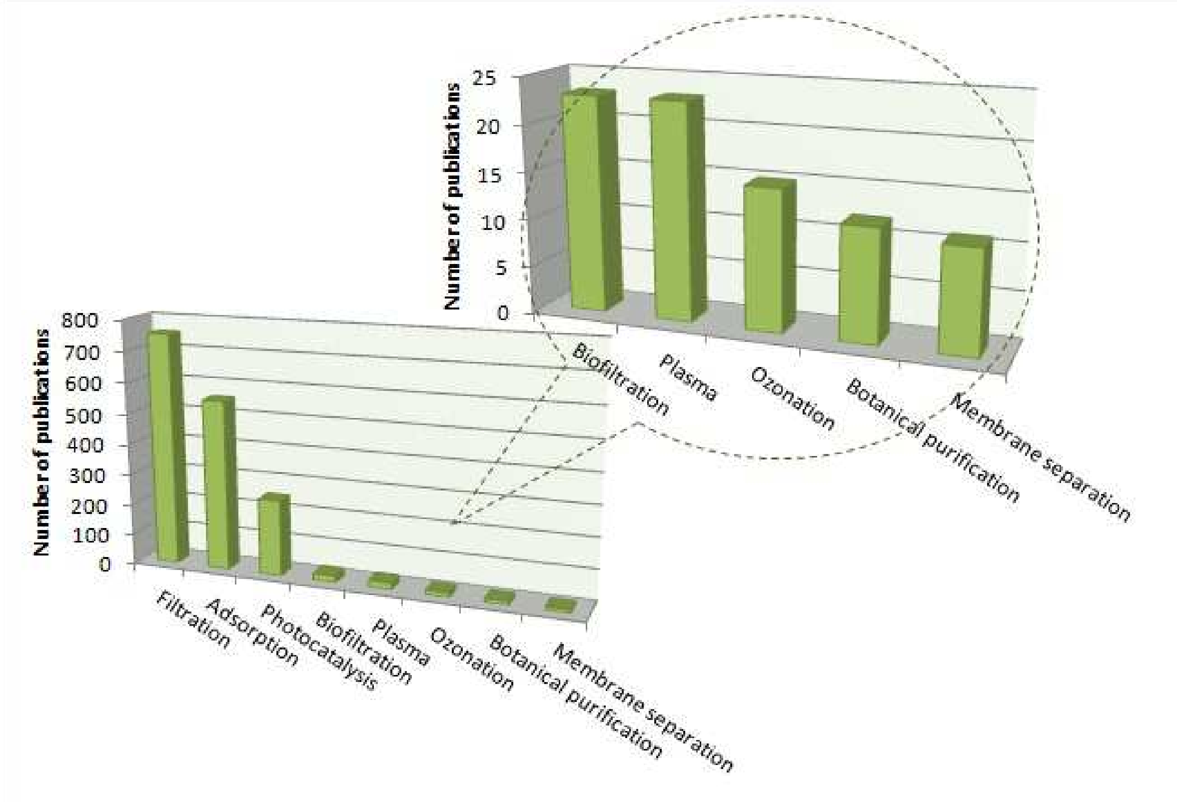


Figure 1.1 Number of articles published on indoor air treatments from 2002 to 2012 (Scopus 2012)

In this context, Weschler *et al.* (2009) found that indoor ozone concentrations increased last year as a consequence, among others, of the use of devices that generate ozone (ionic air cleaners, ozone generators, and electrostatic precipitators). This finding explains the increase in secondary emissions of carbonyl compounds as they are produced by reactions between ozone and unsaturated hydrocarbons (Uhde and Salthamer, 2007). For instance, Zhang *et al.* (1994) observed the formation of compounds such as formaldehyde, formic acid, benzaldehyde and acetic acid from reactions between ozone and some volatile organic compounds (styrene, limonene and 4-vinylcyclohexene). These facts and the increasing concern in building energy savings are pushing research in the way to find a new better technology to treat chemical indoor pollution. This new technology should focus on preventing the emission of by-products, reducing the energy demand and the operating costs (Siegel, 2015). The extensive literature review demonstrates that there are still challenges that have to be addressed in the area of indoor air pollution treatment.

Additionally, technological developments have to consider indoor air pollution as a complex subject involving myriad of chemical species (incompletely identified) influenced by environmental conditions which vary in space and time. Furthermore, chemical species are present at low concentrations and have diverse physical-chemical properties. Among these, the volatile organic compounds (VOC) are major contributors to the deterioration of IAQ. They are emitted by different indoor activities including cooking, burning of candles, open fireplaces, body care, house cleaning, washing, renovation work, the use of electronic devices such as photocopiers or printers, etc. (Salthammer and Bahadir, 2009; Sarigiannis *et al.*, 2011).

These compounds (VOCs) are associated with allergies and adverse respiratory effects (Colman Lerner *et al.*, 2012) and some of them have been classified as carcinogenic to humans (benzene, formaldehyde) by the International Agency for Research on Cancer (IARC, 2015). Many studies attempt to find an efficient technology to treat indoor VOCs contaminant (Hodgson A.T. *et al.*, 2007; Mo J. *et al.*, 2009; Lu Y. *et al.*, 2010; Lu *et al.*, 2012; Zhong L. *et al.*, 2013; Soreanu *et al.*, 2013). Recently, biotechnologies appeared as good alternatives due to their economical and environmental attributes (Lu *et al.*, 2010; Soreanu *et al.*, 2013).

Among the biological technologies, biofiltration seems to be the most attractive technique since it has been described as a competitive technology for the VOCs treatment, according to its simple operation, low operating and maintenance costs (Rojo *et al.*, 2012) and its ability to cope with moderately hydrophobic pollutants (Estrada *et al.* 2011). Its principle is based on the biodegradation of pollutants by the microorganism developed onto a wet packing material throughout which a contaminated air stream passes. A complex combination of physicochemical and biological phenomena takes place to finally convert pollutants into innocuous compounds (mostly CO_2, H_2O and biomass).

In this context, the main objective of this research thesis focuses on the study of biofiltration and the combination of this technology with adsorption onto activated carbon (hybrid process) to treat indoor VOCs. From the VOCs, benzene, toluene, ethylbenzene and m-, p-, o-xylenes (BTEX group) are the largest group associated with human-health effects (Lawrence, 2006). Their main indoor sources are paints, cigarette smoke, building materials and vehicle emissions that are transferred from attached garages and/or outdoors (Wheeler *et al.*, 2013). Until now, most of the indoor air biofiltration studies have focused on the treatment of a single pollutant. In this thesis, ternary or binary systems of VOCs were also used to assess the performance of the treatment systems: toluene and p-xylene were considered in the study presented in Chapter 4; toluene, ethylbenzene and p-xylene were treated by biofiltration in Chapter 6 and toluene was used as a target compound in the study presented in Chapter 5.

As in recent years, an increasing trend towards the utilization of industrial residues has been detected (Mathur, 2007), organic packing materials were tested in this thesis: a compost obtained by mixing pig manure and sawdust and the luffa sponge which is a natural material from the *Cucurbitaceae* plant family were used as packing materials in the study of Chapter

4; a mature green waste compost was used in biofiltration stage in the research presented in Chapter 5 and two soils recovered from construction sites were characterized and tested in the study of Chapter 6.

The effects of several parameters on the performance of both systems (biofiltration and hybrid system) were analyzed along the different experimental studies. Thus, several VOCs concentrations were tested (background and peak concentrations), packing material properties were analyzed and operational disruptions were operated in order to test the robustness of the systems and to select the most suitable for indoor environments.

In brief, biotechnologies and specially hybrid systems turned out to be good alternatives in the treatment of indoor air pollution according to the conditions tested during this research study.

References

Chithra VS, Shiva-Nagendra SM. 2012. Indoor air quality investigations in a naturally ventilated school building located close to an urban roadway in Chennai, India. Building and Environment 54:159–167

Colman Lerner JE., Sanchez EY., Sambeth JE., Porta AA. 2012. Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina. Atmospheric Environment. 55: 440-447.

Consumers Union of U.S., Inc. 2007. Air Purifiers: Filtering the claims. Consumer Reports, December, 48-51.

Estrada JM., Kraakman NJR., Lebrero R., Muñoz R. 2012. A sensitivity analysis of process design parameters, commodity prices and robustness on the economics of odour abatement technologies. Biotechnology Advances. 30: 354–1363.

Fisk WJ. 2000. Health and productivity gains from better indoor environments and their relationship with building energy efficiency, Annual Review of Energy and the Environment. 25: 537-566.

Geiss O, Giannopoulos G, Tirendi S, Barrero-Moreno J, Larsern BR, Kotzias D. 2011. The AIRMEX study - VOC measurements in public buildings and schools/kindergartens in eleven European cities: Statistical analysis of the data. Atmospheric Environment. 45: 3676-3684.

Hodgson AT, Destaillats H, Sullivan DP, Fisk WJ. 2007. Performance of ultraviolet photocatalytic oxidation for indoor air cleaning applications. Indoor Air. 17: 305–316.

IARC-International Agency for Research on Cancer. 2015. Monographs on the Evaluation of Carcinogenic Risks to Humans. Agents Classified by the IARC Monographs, volumes 1–113 Lyon, France. http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf. Accessed April 2, 2014.

Lawrence S.J., 2006, Description, properties, and degradation of selected volatile organic compounds detected in ground water — A Review of Selected Literature: Atlanta, Georgia, U. S. Geological Survey. 2006. Open-File Report 2006-1338, 62 p., a Web-only publication at http://pubs.usgs.gov/ofr/2006/1338/. (consulted on April 15th 2015)

Liébana EA, Calleja AH. 1998. El aire en interiores: métodos de control y depuración. Enciclopedia de Salud y Seguridad en el Trabajo 45:7-11 www.insht.es/InshtWeb/Contenidos/Documentacion/TextosOnline/EnciclopediaOIT/tomo2/45.pdf Accessed 22 June 2012

Lu Y, Liu J, Lu B, *et al.* 2010. Study on the removal of indoor VOCs using Biotechnology, Journal of Hazardous Materials. 182: 204-209.

Lu Y, Wang D, Wu Y, Ma C, Zhang X, Yang C. 2012. Synergistic Effect of Nanophotocatalysis and Non thermal Plasma on the Removal of Indoor HCHO. International Journal of Photoenergy. 2012: ID 354032.

Mathur AK., Majumdera CB., Chatterjee S. 2007. Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media. Journal of Hazardous Materials. 148: 64–74.

Mendell MJ. 2003. Indices for IEQ and building-related symptoms. Indoor Air. 13: 364–368.

Mo J, Zhang Y, Xu Q, Lamson JJ, Zhao R. 2009. Photocatalytic purification of volatile organic compounds in indoor air: A literature review. Atmospheric Environment. 43: 2229-2246.

Rojo N., Muñoz R., Gallastegui G., Barona A., Gurtubay L., Prenafeta-Bolduc FX., Elias A. 2012. Carbon disulfide biofiltration: Influence of the accumulation of biodegradation products on biomass development. Journal of Chemical Technology and Biotechnology. 87: 764–771.

Salthammer T., Bahadir M. 2009. Occurrence, Dynamics and Reactions of Organic Pollutants in the Indoor Environment. Clean Journal. 37 (6): 417 – 435.

Sarigiannis DA, Karakitsios SP, Gotti A, Liakos IL, Katsoyiannis A. 2011. Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. Environment International 37:743–765

Siegel JA. 2015. Primary and secondary consequences of indoor air cleaners. Indoor Air. *doi:10.1111/ina.12194*

Soreanu G., Dixon M., Darlington A. 2013. Botanical biofiltration of indoor gaseous pollutants – A mini-review. Chemical Engineering Journal. 229: 585–594.

Uhde E., Salthammer T. 2007. Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry. Atmospheric Environment. 41: 3111–3128.

Wheeler AJ., Wong SL., Khoury C., Zhu J. 2013. Predictors of indoor BTEX concentrations in Canadian residences. Statistics Canada. Catalogue no. 82-003-X. Health Reports. 24 (5): 11-17.

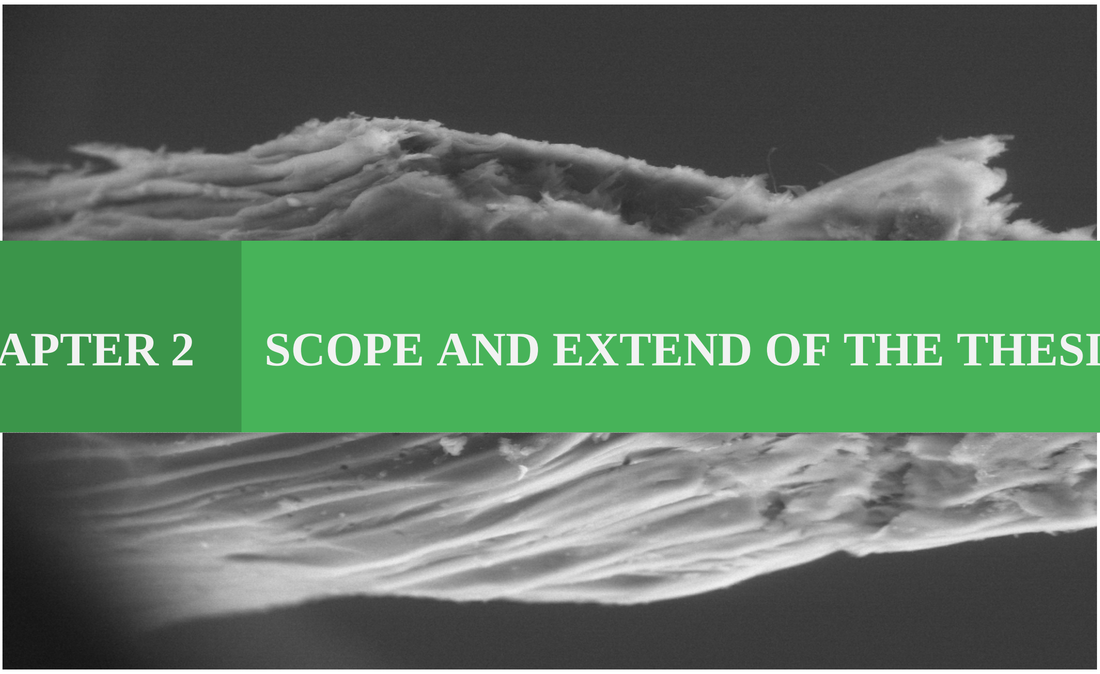
Weschler CJ. 2009. Changes in indoor pollutants since the 1950s. Athmospheric Environment 43:153-169.

World Health Organization (WHO). 2014. Public Health, Environmental and Social Determinants of Health (PHE). Geneva. http://www.who.int/phe/health_topics/outdoorair/databases

Workers' Compensation Board (WCB). 2005. Indoor Air Quality, a guide for building owners, managers and occupants. WCB Publications. http://www.worksafebc.com/publications/health_and_safety/by_topic/assets/pdf/indoor_air_bk89.pdf

Zaatari M, Nirlo E, Jareemit D, Crain N, Srebric J, Siegel J. 2014. Ventilation and indoor air quality in retail stores: A critical review (RP-1596). HVAC&R Research. 20: 276–294.

Zhang J., Wilson W.E., Lioy P.J. 1994. Indoor air chemistry: formation of organic acids and aldehydes. Environmental Science & Technology. 28 (11): 1975-1982.



CHAPTER 2 SCOPE AND EXTEND OF THE THESIS

2. SCOPE AND EXTEND OF THE THESIS

Conventional techniques in the treatment of gaseous effluents which have been developed in recent years for the industry are not suitable for the problem of indoor air purification. The indoor air is characterized by the presence of a wide variety of contaminants, with different physicochemical properties, at very low concentrations that sometimes are higher than the limits or guideline values corresponding to an acceptable health risk. The phenomena involved in the existing treatment processes today are affected by these specificities of the indoor air.

Accordingly nowadays, there is no technology capable, alone, of treating indoor air without collateral effects (byproducts' generation, high energy consumption, etc.). The diversity of these pollutants that have significantly different physicochemical properties, leads to the need of coupling different technologies to achieve satisfactory cleaning performance for a sufficiently wide spectrum of pollutants.

In this context, this project aims at regaining the quality of indoor air quality (IAQ) by broadening the spectrum of pollutants, to which the currently treating technologies are addressed , specially, to the pollutants belonging to the chemical family of Volatile Organic Compounds (VOCs), very present and often harmful, but much less studied than NO_x and CO.

The main objective of this thesis was to develop two systems to treat indoor VOCs, working at representing conditions of those found in indoor environments (very low concentrations of a mixture of pollutants). As this thesis is a joint supervision between the Université de Pau et des Pays de l'Adour (UPPA) in France and the University of the Basque Country (UPV) in Spain, its development was carried out on both sites. In the UPPA, the Laboratory of Thermal, Energy and Processes took part in this study and the other part was carried out in the Biofiltration research group at the Chemical and Environmental Engineering Department (IQMA) of the UPV. Specific goals to achieve the objective are:

- Review the current treatment technologies (commercialized or under research) for indoor air pollution.
- Selection of some VOCs representatives of indoor air pollution based on literature review.
- Generation of a model effluent whose pollutant concentrations are on the order of ppb (representing pollution background of indoor air) at the LaTEP site. In the IQMA

laboratory, generation of pollution peaks models (ppm range) corresponding to specific activities in residences and/or special confined spaces.
- Selection of a suitable support for biofiltration and adsorption and set of the best operational conditions for a biofiltration system and a hybrid system (biofiltration-adsorption).
- Design and implementation of two complementary systems (in Spain and in France).
- Study the influence of different operating parameters and environmental conditions on the implemented systems.
- Study the effectiveness and safety of the biofilter and the hybrid system. Determination of generation of by-products and particle emissions.
- Design approach of the hybrid system.

In brief, the overall objective of this thesis can be schematized as shown in Figure 2.1:

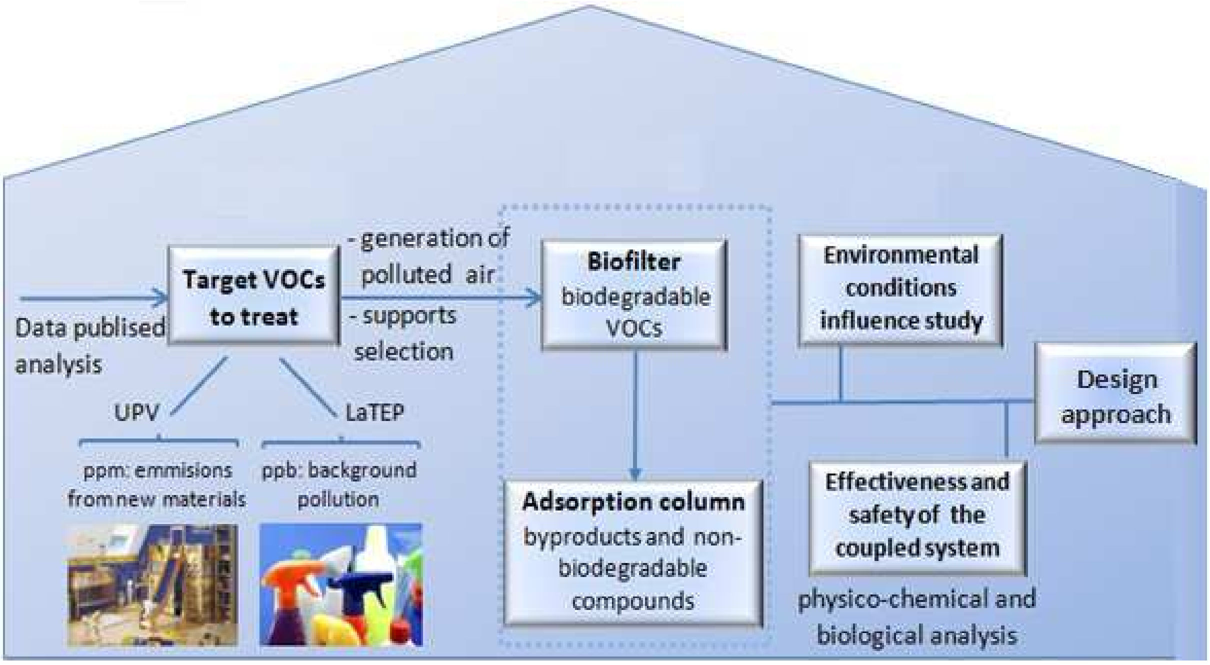


Figure 2.1 Schematization of the thesis study.

CHAPTER 3

A REVIEW OF INDOOR AIR TREATMENT TECHNOLOGIES

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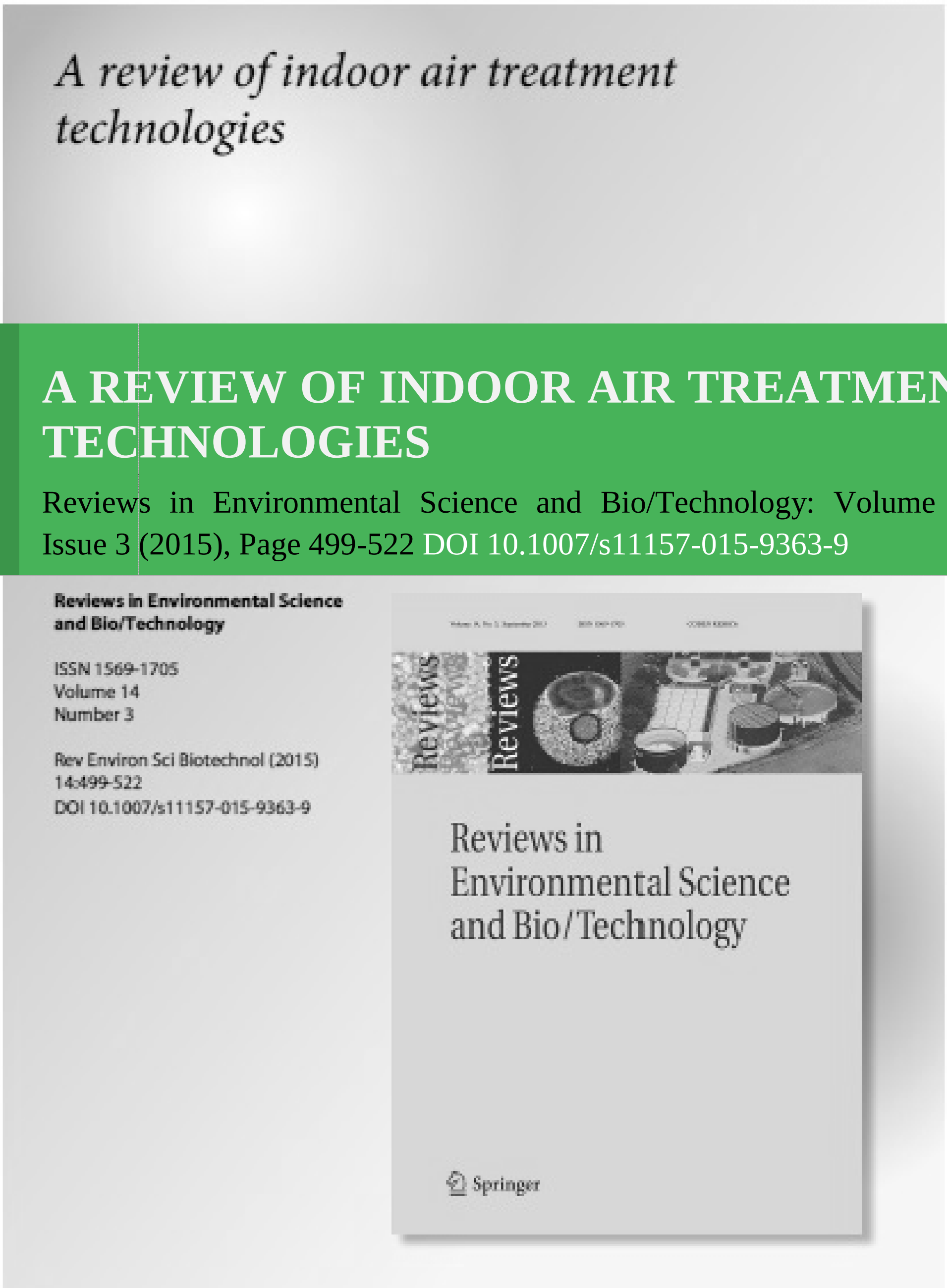

A review of indoor air treatment technologies

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3. A REVIEW OF INDOOR AIR TREATMENT TECHNOLOGIES

3.1. Abstract

Indoor air pollution is a complex issue involving a wide diversity and variability of pollutants that threats human health. In this context, major efforts should be made to enhance indoor air quality. Thus, it is important to start by the control of indoor pollution sources. Nevertheless, when the suppression or minimization of emission sources is insufficient, technically unfeasible, or economically unviable, abatement technologies have to be used. This review presents a general overview of single treatment techniques such as mechanical and electrical filtration, adsorption, ozonation, photolysis, photocatalytic oxidation, biological processes, and membrane separation. Since there is currently no technology that can be considered fully satisfactory for achieving "cleaner" indoor air, special attention is paid to combined purification technologies or innovative alternatives that are currently under research and have not yet been commercialized (plasma-catalytic hybrid systems, hybrid ozonation systems, biofilter-adsorption systems, etc.). These systems seem to be a good opportunity as they integrate synergetic advantages to achieve good indoor air quality.

3.2. Introduction

People's lifestyles have changed dramatically over the past forty years, particularly in the industrialized nations. Increasing urbanization, technological development and specialized occupational activities are responsible for the long time people spend indoors (i.e., in offices, public transportation facilities, schools and shopping centres). Indoor air quality (IAQ) has therefore become an issue of great concern, as the prevalence of sick building syndrome (SBS), building related illness (BRI), and multiple chemical sensitivity (MCS) has been reported in recent decades (Lan *et al.*, 2011; Mallawaraachchi and De Silva, 2014). In addition, the World Health Organization (WHO) recently reported that air pollution caused around seven million premature deaths in 2012, of which 4.3 million were related to indoor air pollution (WHO 2014).

Any improvement in IAQ has been shown to directly benefit health and productivity, with the associated economic benefits. About 235 million people suffer from asthma in the world, and the socioeconomic cost attributable to indoor air pollutants in France alone is estimated at 20 billion euro per year (WHO, 2013; ANSES, 2014). Fisk *et al.* (2011) have also estimated the economic benefits of implementing scenarios for improving indoor environmental quality in the USA. These benefits are calculated to amount to approximately US$ 20 billion. Although these quantitative estimates are difficult to confirm with any certainty, the opportunity for substantial benefits is clear.

Regarding the regulation of IAQ in recent years, WHO singled out IAQ as one of its concerns in public health in 1979, and in 2010 specific indoor air quality guidelines were published by this organization (WHO 2010). Other organizations in several countries have also adopted guidelines for certain priority indoor air pollutants that represent a risk for human health; some guidelines are listed in Table 3.1. In France, new regulations have been established concerning IAQ in public buildings. French Decree No. 2011-1727 establishes concentration values for formaldehyde and benzene. As far as formaldehyde is concerned, limit concentrations of 30 μg/m^3 and 10 μg/m^3 are to be introduced in 2015 and 2022, respectively. The limit concentration for benzene in 2016 will be 2 μg/m^3 (the current limit is 5 μg/m^3) (Ministry of the Ecology, Suitable Development, Transport and Accommodation in France 2011a). Concomitantly, French Decree No. 2011-1728 imposes the obligation to measure periodically those concentrations in public building. IAQ control in public buildings receiving children under the age of six will be compulsory as of 2015, followed in 2018 by primary schools, by high schools and leisure centres in 2020, and by other public buildings in 2023 (Ministry of the Ecology, Suitable Development, Transport and Accommodation in France 2011b).

Table 3.1 Indoor air quality guidelines in different countries

France (ANSES 2014b)	**Value (μg m^{-3})**	**Averaging time^a**
Formaldehyde	50	2 h
	10	>1 year
Carbon monoxide	$10x10^3$	8 h
	$30x10^3$	1 h
	$60x10^3$	30 min
	$100x10^3$	15 min
Benzene	30	1-14 days
	20	14 days to 1 year
	10	> 1 year
	0.2	whole life; risk level of 10^{-6}
	2	whole life; risk level of 10^{-5}
Naphtalene	10	> 1 year
Trichloroethylene	800	14 days to 1 year
	2	whole life; risk level of 10^{-6}
	20	whole life; risk level of 10^{-5}
Tetrachloroethylene	1380	1-14 days
	250	> 1 year
Nitrogen dioxyde	200	2 h
	20	> 1 year
Acrolein (2-propenal)	6.9	1 h
	0.8	> 1 year
Acetaldehyde (ethanal)	3000	1 h

	Value (µg m^{-3})	**Averaging time[a]**
	160	> 1 year
WHO (WHO 2010)		
Formaldehyde	1000	30 min
Carbon monoxide	7x10^3	24 h
	10x10^3	8 h
	35x10^3	1 h
	100x10^3	15 min
Benzene	17	whole life; risk level of 10^{-4}
	1.7	whole life; risk level of 10^{-5}
	0.17	whole life; risk level of 10^{-6}
Naphtalene	10	annual average
Trichloroethylene	230	whole life; cancer risk level of 10^{-4}
	23	whole life; cancer risk level of 10^{-5}
	2.3	whole life; cancer risk level of 10^{-6}
Tetrachloroethylene	250	annual average
Nitrogen dioxyde	200	1 h
	40	annual average
PAH (Benzo(a)pyrene)	1.2	whole life; cancer risk level of 10^{-4}
	0.12	whole life; cancer risk level of 10^{-5}
	0.012	whole life; cancer risk level of 10^{-6}
Canada (Health Canada 2014)		
Formaldehyde	50	8 h
	123	1 h
Carbon monoxide	11.5x10^3	24 h
	28.6x10^3	1 h
Naphtalene	10	24 h
Toluene	2.3x10^3	24 h
	15x10^3	8 h
China (Stranger 2007)		
Sulfur dioxide (SO2)	150	24 h
Nitrogen dioxide (NO2)	100	24 h
Carbon monoxide (CO)	5000	24 h
Formaldehyde	80	1 h
Benzene	90	1 h
Benzo(a) pyrene	0.001	24 h
TVOC	600	24 h

[a] The WHO and the ANSES take the plausibility of a human cancer risk to estimate a risk rather than a safe level for benzene, thrichloroethylene and benzo(a)pyrene.

Indoor air pollution (IAP) basically refers to a variety of chemical, biological and physical agents that pose a health threat or cause discomfort. In general terms, IAP can be classified as follows:

3.2.1. Pollution by particulate matter (PM)

Particulate matter refers to a wide range of particles (solid or even liquid) that are small enough to be airborne, and therefore inhaled by people. The particles vary considerably in size, but the smaller particles pose the highest health threat because they can travel deepest into the lungs. Ultra-fine particles with a diameter between 5.6 and 560 nm are usual in indoor air, although the amount of particles of 10 μm or 2.5 μm or less in diameter (PM_{10} and $PM_{2.5}$, respectively) is more frequently measured. There are very few studies on the health effects of indoor PM_{10} and $PM_{2.5}$, in comparison to the higher amount of studies on outdoor particles, but those available link PM to respiratory complaints (Weichenthal *et al.* 2007; Lin *et al.* 2011; Taner *et al.* 2013).

The most notorious pollutant within this family is asbestos, which has been used on a large scale in a number of materials for construction. All forms of asbestos (chrysotile, crocidolite, amosite, tremolite, actinolite, and anthophyllite) have been found to cause mesothelioma and cancer of the lung, larynx, and ovary (International Agency for Research on Cancer 2012). The WHO stated that at least 107 000 people die each year globally due to asbestos-related diseases. Therefore, many countries have already taken action to prohibit the use of all forms of asbestos, and other countries have imposed strict regulations to limit exposure (WHO 2014). In France, a complete ban on asbestos was adopted since 1997, and at the European level, all extraction, manufacturing, and processing of asbestos fibres was prohibited in 1999 by Directive 99/77/EC (ANSES 2013). The Australian government published a guide for householders and the general public to safely manage the risks arising from any occasional encounters with asbestos indoors or around their homes (Environment Health Standing Committee 2013) and the US Environmental Protection Agency (EPA) provides a listing of the laws and regulations governing asbestos (US EPA 2014).

3.2.2. Biological pollution

It is essentially composed of animal allergens (dust mites and certain proteins contained in excrement and hair), bacteria, mould, fungi, spores, endotoxins, mycotoxins, and all kinds of living organisms with highly variable and complex characteristics. Recent studies have found a close relationship between these bioaerosols and more serious episodes of asthma, rhinitis and conjunctivitis (Casset and Braun 2010). In fact, aerosols are responsible for about 5-34% of all indoor pollution, and their abundance depends on indoor moisture and temperature conditions (Srikanth *et al.* 2008; Nazaroff, 2013).

3.2.3. Physical pollution

Although several physical agents may be mentioned in this section, only temperature and electromagnetic fields (EMFs) will be addressed in detail. Air temperature has a significant impact on comfort, and thus on the perception of indoor air quality. Besides the discomfort they cause, high temperature and excessive humidity promote the spread of microorganisms (responsible for the aforementioned biological pollution), and may also favour secondary chemical reactions among the chemical compounds present in indoor air.

As far as EMFs are concerned, they are generated when charged particles are accelerated by alternating current in electrical conductors. There are two main forms of EMFs: radiofrequency (RF)-EMFs, which are produced by mobile phones and other communication devices, and extremely low-frequency (ELF)-EMFs, which are produced by power lines and many domestic appliances. As yet, no link has been found between health issues and electromagnetic pollution, but some agencies, such as "The Architectural and Transportation Barriers Compliance Board" in the USA, have reported an increasing number of complaints from people who suffer adverse effects derived from electromagnetic radiation (Kubba 2010).

3.2.4. Chemical pollution

This group comprises all the chemical compounds that can be found in indoor air. Over 400 different compounds have been identified, with very wide variations in both concentration and properties (Gale *et al.* 2009).

This article presents a review of the state-of-the-art in the study of indoor chemical pollution and technological alternatives for its effective treatment. Special attention is paid to the research on combined systems, as they seem to be a promising alternative for improving indoor air quality.

3.3. Indoor pollution sources

The pollutants that indoor occupants are exposed to today are substantially different from those they experienced 40 years ago because pollution sources have dramatically changed (Weschler 2009). Old construction materials considered to be “inert” have now been replaced by complex new materials such as polymers, chemically treated materials, and technologically developed paints, amongst others. Today, another feature of this pollution is related to the development of new building techniques and designs devoted to effective energy saving. Airtight or sealed constructions and an inappropriate ventilation rate in these new buildings are singled out as being responsible for the deterioration in indoor air quality.

Many studies reveal that building materials and human indoor activities are major sources of indoor pollution (Fromme *et al.* 2013; Gunschera *et al.* 2013). The sources of chemical pollution can be grouped into three categories:

3.3.1. Endogenous sources

Two endogenous sources may be mentioned: permanent sources and occasional sources. Regarding permanent sources, these include emissions from building materials, hardwood, plywood, laminated materials, insulators, adhesives, and paints and varnishes. According to some studies, approximately 40% of the overall air pollution inside buildings is attributed to building materials (Missia *et al.* 2010). The occasional sources are related to human activities involving the use of different products for cleaning, disinfection, gardening, and personal care. Cooking is a major source of pollutants in dwellings and restaurants, with hospitals, public transport or offices producing their own specific pollution. Nevertheless, the impact of these sources is informed by other variables, such as standard of living, population, climate, and geographical location.

Human metabolism is also considered an endogenous source of contamination: isoprene and acetone are the most prominent pollutants included in the list of the 199 volatile organic compounds (VOCs) identified with reasonable certainty in human breath, with some of them being associated with diseases such as diabetes or lung cancer (De Lacy Costello *et al.* 2014).

3.3.2. Reaction products in an indoor environment

In addition to the direct emission of primary pollutants from indoor sources, the formation of secondary pollutants from indoor gas-phase reactions is a very significant secondary source. The variety of chemicals in the different materials used in building and furnishing may undergo chemical reactions on the material´s surface or in the gas phase. Gaseous compounds with C = C bonds are prone to react with O_3, NO_x, OH radicals and other gases (Uhde and Salthammer 2007). The ozonolysis of alkenes is reported to be a major pathway for OH formation indoors, and the photolysis of HONO makes a greater contribution to indoor OH than previously assumed (Gligorovski and Weschler 2013). Thus, the oxidative capacity of indoor atmospheres has a significant impact on the level of indoor pollution, although further research is required on the mechanisms and products of oxidation processes.

3.3.3. Transfer from the outdoor environment

Although sources of outdoor air pollution are both natural and anthropogenic, the most common sources derived from human activities are industry, road traffic, power stations, and the combustion of fossil fuels, such as coal, oil and gas. Regardless of their outdoor origin, several compounds such as acrolein have been found to concentrate indoors (Liu *et al.* 2006).

3.4. Chemical pollutants

An increasing variety of chemical compounds has been found in indoor air. The main chemical pollutants detected in indoor air are as follows:

3.4.1. Carbon dioxide (CO_2)

Carbon dioxide is a metabolic product frequently used as an indicator of the overall level of air pollution and the need for ventilation in an occupied space. The maximum recommended occupational exposure limit is 5000 ppmv for an eight-hour workday (time weighted average) (OSHA 2012). A typical indoor CO_2 concentration range of between 350 and 2500 ppmv has been reported as safe (Sappänen *et al.* 1999). Nevertheless, Erdmann and Apte (2004) have found statistically significant associations between the mucous membrane and lower respiratory building-related symptoms, with increasing values in the difference between indoor and outdoor CO_2 concentrations on a workday basis.

3.4.2. Inorganic gases

Inorganic gases are mainly represented by gaseous compounds such as carbon monoxide (CO), nitrogen oxides (NO_x) and sulfur dioxide (SO_2) whose concentrations are heavily influenced by outdoor levels (Weschler 2009). Nevertheless, combustion appliances, tobacco smoke and the burning of incense can increase indoor levels. In Canada, CO levels as high as 115 mg/m^3 have been found in some domestic kitchens immediately after cooking with an unvented gas stove (Alberta Health 2012). The health effects associated with inhaled CO vary with its concentration and exposure. At low levels (120-520 ppmv), CO has minor effects that are often confused with a cold. These symptoms include headache, dizziness, disorientation, nausea, and tiredness (Kotzias *et al.* 2005).

The sum of nitric oxide (NO) and nitrogen dioxide (NO_2) is commonly called nitrogen oxides or NOx. NO_2 is of concern in indoor air due to its irritating effects on the respiratory tract (Wainman 2001). Conversely, NO is not considered particularly toxic at typical concentrations. Indoor NO_2 concentrations normally range from 30 to 40 ppbv, with occurrences as high as 100 ppbv (Wainman 2001). Indoor concentrations of SO_2 range from 0.5 to 32 µg/m^3 (Brauer *et al.* 2002). The effects of SO_2 exposure include difficulty in breathing, irritation of the throat and eyes, and coughing (WHO 2000).

3.4.3. Ozone (O_3)

Ozone is a photochemical reaction product in polluted atmospheres, but it can also be released by devices such as air ionic purifiers, ozone generators, electrostatic filters, printers and copiers, among others. Low amounts of O_3 (80-120 ppbv) can cause eye irritation, visual disturbances, headaches, dizziness, dry mouth and throat, chest tightness, and coughing (Sittig, 1991). Exposure to relatively high concentrations of this gas has been associated with chest pain, coughing, difficulty in breathing, and respiratory tract irritation, as well as the worsening of respiratory diseases such as asthma (US EPA 1997). The WHO average guideline value is 100 μg/m^3 for an eight-hour day.

3.4.4. Organic compounds

Organic compounds comprise a group of hundreds of organic chemicals, but most of them are present at very low concentrations (parts per billion) (Weschler 2009). The World Health Organization (WHO 1989) classifies organic compounds by their normal boiling point (<0 °C to 50-100 °C) into very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), with a boiling point of 50-100 °C to 240-260 °C, and semivolatile organic compounds (SVOCs) with a boiling point of 240-260 °C to 380-400 °C. Some of these compounds are associated with allergies and adverse respiratory effects (Sundell 2004), and others have been classified as known human carcinogens (Weschler 2009).

Among the variety of indoor pollutants, Gallego *et al.* (2009) have identified 130 different VOCs in private homes, with alkanes being the largest group (32%), followed by aromatic hydrocarbons (17%) and esters and alkenes (7%).

The ratio between indoor and outdoor concentrations for certain common compounds in some particular environments reveals the main source (Table 3.2). Indoor/outdoor ratio values higher than 30 in private homes have been reported for acetaldehyde and xylene, which are directly linked to tobacco smoke and paints, respectively (Sarigiannis *et al.* 2011). The presence of toluene is also widespread in schools, where a ratio of 25.2 has been found. As an indicator of the pollutants reported in furniture malls, benzene has a ratio of 7.9.

Huang *et al.* (2011) have studied the environment in two households during cooking activities; the first one used a fuel consisting of 49% hydrogen and 28% methane, and the other one used a fuel with 75% propane and 25% butane. Elevated amounts of CO2 were measured in both homes, but the amount of CO was higher for the one that used propane and butane, which may be related to incomplete combustion. The presence of C2 compounds (ethane, ethene, and ethyne) in both homes was associated with the heating of meat products and fat. Activities such as roasting coffee beans emit high quantities of acetaldehyde (5233 ppbv) and other compounds, such as hydrogen sulfide (2398 ppbv) and methanethiol (2070 ppbv) (Kabir *et al.*, 2010). Other compounds present in kitchens are formaldehyde, toluene, hexanal, and acetone.

Other compounds with high ratios are shown in Table 3.3. The most noticeable cases involve α-pinene and d-limonene, which have been reported in homes with indoor/outdoor (I/O) ratios of up to 145 and 97.3, respectively. Based on its characteristically pleasant odour, d-limonene is used as a flavour and fragrance additive in food, household cleaning and polishing products, as well as in perfumes and personal care products, and can be found in solvents. α-Pinene is a naturally occurring terpene, which is emitted indoors by wood-based products, or contained in aerosol paint concentrates, cleaning and hygiene products, varnish removers, waterproofing solvents, and flavours (Geiss *et al.* 2011).

Table 3.2 Indoor/outdoor ratio for certain common organic compounds in several indoor environments

	Indoor/outdoor ratio					
Indoor environment	**Toluene**	**Acetaldehyde**	**Xylene**	**Formaldehyde**	**Benzene**	**Ethylbenzene**
Public building[a]	0.9-4.1	0.7-7.0	0.7-11.8	0.8-10.7	0.1-1.2	0.9-8.3
Schools[a]	1.2-25.2	2.4-14.8	0.9-6.7	4.2-10.7	1.0-3.1	1.1-3.4
Houses[a]	1.6-12.8	2.3-31	1.2-30.4	5.0-16.4	0.6-2.6	1.1-24
Furniture mall[b]	5.7	2.9	7.6	6.9	7.9	7

a Missia *et al.* 2010
b Jiang *et al.* 2013

Table 3.3 Indoor concentrations of particular pollutants and indoor/outdoor ratio (Geiss *et al.* 2011)

Compound	**Concentrations (μg m^{-3})**			**Indoor/outdoor ratio**
	Public buildings and/or schools	**Houses**	**Outdoor**	
d-limonene	9.4	29.2	0.3	31.3-97.3
α-pinene	3.2	14.5	0.1	32-145
1-butoxy-2 propanol	4.7	12.5	1.6	2.9-7.8
acetone	5.7	11.6	0.3	19-38.7
n-decane	14.4	17.3	6.2	2.3-2.8
hexanal	16.4	32.3	0.9	18.2-35.9

Indoor environments in hospitals have their own specific contaminants, such as ethylene oxide, which is used for sterilization (Wang *et al.* 2007). Offices where photocopiers, computers and other devices are used also have specific pollutants, such as ozone, PM_{10}, acetone, ethylbenzene, xylene, and styrene (Lee *et al.* 2001). Other examples of indoor VOC concentrations at different locations are shown in Table 3.4.

As better analytical instruments are being developed, sampling procedures are being standardized and instrument sensitivities improved, the number and type of compounds identified and quantified indoors are continuously increasing (Weschler 2009; Panagiotaras *et al.* 2014). Bearing in mind the different types of VOC compounds and the diversity in their physico-chemical properties, a series of protocols and methodologies have been developed in order to achieve common indoor air sampling strategies and VOC quantitative analysis (Bacaloni *et al.* 2005; Panagiotaras *et al.* 2014).

Table 3.4 Indoor concentrations of common organic compounds in different environments ($\mu g\ m^{-3}$)

Environment	TVOC[a]	Toluene	Xylenes	Formaldehyde	Benzene	Ethylbenzene	References
Living room	12.14-84.32	6.35-28.27	1.63-14.56	-	0.52-10.26	1.31-11.08	Ohura *et al.* 2006
Bedroom	9.17-86.14	4.72-31.04	1.18-15.47	-	0.35-11.13	0.98-11.61	
Kitchen	12.35-62.92	6.38-23.95	1.69-9.53	-	0.5-9.92	1.34-8.10	
Apartment	199.69	31.81	9.64	-	3.09	3.59	Rehwagen *et al.* 2003
Medical centre	931.1	61.5	21.7	24.1	5.1	12.1	Lee *et al.* 2011
Children’s hospital	-	5.5-8	3.6-3.9	15-10.9	1.4-2.1	1.3	Roda *et al.* 2011
Office	-	5.7-58.0	4.6-37.0	11.0-66.0	4.7-12.0	-	Wang *et al.* 2007
Library	1268.2	32.4	6.3	34.8	4.7	6.3	Lee *et al.* 2011
Large store	1954.4	83	4.2	98.1	6.8	4.8	Lee *et al.* 2011
Primary school	124-3028	9.3-34.8	<13.5	-	3.6-19.8	3.3-5.1	Mentese *et al.* 2012
Indoor parking	1412.1	91.1	13.7	49.5	16.6	11.4	Lee *et al.* 2011
Underground station	1073.6	65.4	15.1	33	5.2	13.1	Lee *et al.* 2011
Aircraft	-	4.7-86.5	2.0-12.5	1.7-9.5	0.0-7.3	-	Wang *et al.* 2007
Train	-	7.0-54.0	3.0-9.0	17.0-9.5	2.0-4.0	-	
Bus	-	15.0-39.0	6.0-48.0	-	2.0-6.0	-	
Underground	-	13.0-27.0	5.0-50.0	-	4.0-7.0	-	

[a] TVOC Total Volatile Organic Compounds

3.5. Treatment methods

Three basic strategies may be applied to reduce indoor pollution, and therefore improve IAQ. The first strategy focuses on the control of the pollution source, which can be accomplished by its removal, confinement, or replacement (Liébana and Calleja 1998). A second strategy involves improving the ventilation system by increasing the amount of outdoor air to dilute indoor pollutant concentrations. Nevertheless, this alternative does not necessarily negate the presence of pollutants above a safe limit (Zaatari *et al.* 2014) and may involve the potential risk of simply bringing in more pollutants from the outside, and what's more, it is inconsistent with energy saving policies (Chithra and Shiva-Nagendra 2012). Finally, the third strategy involves the use of purification/treatment technologies.

In sum, a trial set of four simple recommendations for improving indoor air quality has been reported (Nazaroff 2013): 1. Minimize indoor emissions; 2. Keep the area dry; 3. Ventilate well; and 4. Protect against outdoor pollution. When emission sources cannot be controlled or reduced for technical or financial reasons, air cleaning devices need to be used (Ayoko and Wang 2014). The technology behind such devices ranges from simple filters to hybrid treatment systems. Air purification/treatment technologies are briefly described below.

3.5.1. Mechanical Filtration

Mechanical filtration is a simple and extensively used air purification technique for removing suspended particles from indoor air. Filters are essential components in all air conditioning systems, and can capture particles by interception, impact, or diffusion. This technique does not retain gases, although some studies have reported the removal of ozone by up to 36% in indoor air (Zhao *et al.* 2007). Mechanical filters are progressively saturated by particles; thus, pressure loss is increased throughout time in service and, consequently, particle removal efficiency progressively decreases. This problem can be resolved by replacing the filter. The spent filters are new sources of contamination due to the accumulation of material that may promote the growth of harmful microorganisms (Yu *et al.* 2009).

Mechanical filter performance depends on different factors, such as the type of filter (Table 3.5), material used for the filter media, air flow and velocity across the filter, the type of contaminants, and other associated processes (Zhao *et al.* 2007). Additionally, the medium can be treated with viscous substances such as oils to promote the adhesion of particles onto the fibre (US EPA 2009).

Table 3.5 Type of mechanical filters and comparison (Bliss 2005)

Filter type	Efficiency for particles of 0.3-6 µm	Maintenance	Cost	Comments
Flat filters	<5%	Replace every 1-3 months	Very low	Quick saturation and loss of efficacy with use.
Pleated filters	20-50%	Replace every 3-12 months	Low to medium	Higher filtration area.
HEPA (High Efficiency Particle Arresting)	>95%	Change every 1-3 years. Change pre-filters 2-3 times a year	Very high to install + high annual costs	Elimination of spores, dust mites and other allergens.

3.5.2. Electronic filtration

There are two types of electronic filters that involve particle removal. Electrostatic precipitators are medium-cost devices in which particles are ionized and then deflected by an electric field to be trapped on opposite polarity plates. Their maintenance includes the regular removal and cleaning of the plates.

Conversely, ion generators or ionizers are high-cost devices without the need for replacement in which charged ions are dispersed into the air and attached to particles that become chemically charged and trapped in the filters. Nevertheless, those charged particles may adhere to nearby surfaces, such as walls, furniture and draperies, or become attracted to each other by their opposite charges, thereby forming a heavier particle that is deposited on the floor or any other surface (US EPA 2009). According to Bliss (2005), the efficiency of electrostatic filters for a particle range of 0.3–6 µm is over 90%, while this value oscillates between 75–95% for ion generators.

In electronic filters, pressure loss occurs more slowly than in mechanical filters, while other factors, such as certain chemicals, aerosols or high relative humidity, can negatively affect removal efficiency. MacIntosh *et al.* (2008) have observed higher particle removal rates in in-duct electrostatic precipitators compared with either induct or portable HEPA mechanical filters over an 80-minute test period. In contrast, Mølgaard *et al.* (2014) have compared removal rates for particles with diameters above 100 nm, and concluded that air cleaners based on filtration performed 1.4–4.3 and 2.5–7.5 times better than an electrostatic precipitator and an ion generator, respectively.

Although efficient in removing particles, electronic filters can generate hazardous charged particles (Guieysse *et al.* 2008). They may also generate new pollutants such as ozone and other compounds derived from the ionization of VOCs. An ion generator installed in a 27 m^3 residential room by Waring and Siegel (2011) has increased concentrations of ultrafine particles (<0.1 µm), ozone, and to a lesser extent, the by-products of reactions initiated by ozone,-such as aldehydes (formaldehyde and nonanal).

3.5.3. Adsorption

Adsorption has been successfully applied for retaining contaminants on the surface of an adsorbent material, such as activated carbon, zeolites, silica gel, activated alumina, mineral clay, and some polymers. Amongst them, activated carbon and hydrophobic zeolites are the most commonly used because of their large surface area and high adsorption capacity (Huang *et al.* 2003; Kim and Ahn 2012).

The use of an activated carbon filter in a combined heating, ventilation and air conditioning system has been evaluated by Sidheswaran *et al.* (2012). A mixture of VOCs with concentrations in the 20-30 ppbv range was treated, resulting in removal (retaining) efficiencies of 70-80% for most of the VOCs studied (toluene, benzene, o-xylene, 1-butanol, limonene, undecane, and formaldehyde). Cheng *et al.* (2012) have impregnated a zeolite with metallic silver in order to obtain an adsorbent material with antibacterial properties. Over 95% of the bacteria and fungi were removed from indoor air. Jo and Yang (2009) have studied the adsorption of benzene, toluene, ethylbenzene, and xylenes on activated carbon at low concentrations (0.1-1 ppmv). The removal efficiencies obtained herein were close to or above 90%.

Regarding the disadvantages, high relative humidity (resulting in water condensation on the surface pores) and pollutant load variations compromise adsorption efficiency (Jo and Yang 2009). Additionally, not all the compounds adsorb effectively onto the adsorbent surface, and the regeneration of the depleted adsorbents involves significant additional costs (Manéro and Monneyron 2005). Jo and Yang (2009) have concluded that a temperature of 300 °C is required to obtain significant desorption yields (75-95%). Additionally, adsorbents should be regularly replaced in order to avoid the re-emission of the already adsorbed compounds (Liébana and Calleja 1998). Another negative feature is that airborne bacteria can deposit on the adsorbent surface and thrive because of the high biocompatibility of the carbon materials (Pei *et al.* 2013).

Contaminant treatment or destruction is not pursued with this technology, as the pollutant is simply transferred from one phase to another, producing a hazardous waste that must be treated and/or disposed of properly. Nevertheless, Chen *et al.* (2005) have classified sorption filtration as the most effective off-the-shelf commercial technology for the general removal of indoor VOC pollutants. These authors tested fifteen air cleaners representing five different technologies (adsorption, photocatalytic oxidation, ozonation, cold plasma decomposition, and botanical biofiltration) for the removal of a mixture of 16 representative indoor VOCs. All sorption-related products recorded significant removal efficiencies for most pollutants (higher than 90%), and the application of specific sorption media guaranteed the entrapment of the most difficult ones (dichloromethane, formaldehyde, and acetaldehyde). Other technologies were rejected due to their defective implementation in commercial products (photocatalytic oxidation), marginal removal efficiency for certain VOCs (botanical biofiltration), or the generation of significant amounts of ozone (cold plasma decomposition and ozonation).

3.5.4. Ozonation

Ozone (O_3) is an oxidizing agent produced in generators using oxygen from the air. Oxygen molecules (O_2) are exposed to a corona discharge or UV radiation to produce several hundred milligrams per hour of ozone.

The use of indoor ozone generators as air purifiers increased over the 1990s, when they were marketed to consumers for their ability to eliminate odours and microbial agents (Hubbard *et al.* 2005). However, several studies have shown that an indoor ozone concentration in the range 50–100 ppbv (typical exposure limits) does not guarantee the efficient removal of many indoor VOC pollutants, and cannot compete with even moderate ventilation rates (Chen *et al.* 2005; Hubbard *et al.*, 2005; Weschler, 2000). Thus, several public agencies, such as the federal department Health Canada, advise against using air cleaners that are designed to intentionally generate ozone because of concerns about possible health effects from exposure to higher levels of ozone (Health Canada, 2012).

Esswein and Boeniger (1994) have tested an ozone-generating device to treat formaldehyde at concentrations of 2.5 and 1.3 ppmv, with O_3 concentrations of approximately 0.5 ppmv. No reduction in formaldehyde concentration was found using ozone at this concentration. Additionally, Hubbard *et al.* (2005) have reported that the presence of ozone generators in homes contributes to the formation of secondary organic aerosols, especially in the presence of terpenes (usually present in cleaning agents and deodorizers).

3.5.5. UV Photolysis

Ultraviolet (UV) radiation is known to have a removal effect on bioaerosols. It promotes the decomposition of contaminants, such as viruses, bacteria, chemicals, dust mites, animal dander and mould, through a process called photolysis oxidation or UV photolysis. The wavelength range with germicidal effect is between 200 and 365 nm for air or surface disinfection. Nevertheless, photoreactor lamps emitting at 185 and 254 nm wavelengths have been the ones usually tested (Wang *et al.* 2009, Zhao *et al.* 2013).

UV-photolysis treatment is usually conducted at ambient temperature and pressure, which provides an inherent advantage over traditional thermal or chemical oxidation technologies. Furthermore, it is considered to be affordable and efficient (Chen *et al.* 2010). Its efficiency depends on the molar absorptivity of the target gas-phase pollutant at the wavelength used, the intensity of the UV light source, the initial concentrations of the different VOCs present in the waste-gas, relative humidity, and the concentration of added oxidants. Tseng and Li (2005) have reported that airborne virus inactivation was lower at 55% relative humidity than that at 85%.

The application of UV photolysis is limited because of its tendency to produce ozone and radicals with harmful effects (Zhang *et al.*, 2011). In fact, UV radiation only removes some gaseous pollutants and, conversely, it might release toxic photoproducts, apart from being energy consuming (Guieysse *et al.*, 2008). Zhao *et al.* (2013) have studied the intermediates generated during the UV photolysis of naphthalene, and thirteen volatile and five semi-volatile organic by-products were identified, including highly harmful aldehydes (e.g., formaldehyde). Aldehydes are, in fact, recognized as the most important intermediates of toluene and xylene photolysis (Moussavi and Mohseni, 2007). Wang *et al.* (2009) have reported that gaseous chlorobenzene is transformed into chlorophenol, phenol and certain organic acids, such as formic acid and acetic acid.

The photodegradation of α-pinene at concentrations of 500-600 mg/m^3 has been studied by Chen et al (2005). Approximately 28%, 39% and 60% of α-pinene were mineralized at residence times of 18, 45 and 90 s, respectively. Some intermediates such as acetone, 3-hydroxy-α-pinene, glycoaldehyde, acetaldehyde, and 2-methylmalonaldehyde were identified.

3.5.6. Photocatalytic oxidation

Photocatalysis promotes the degradation and mineralization of contaminants in the air by using a semiconductor and an irradiation source in the presence of oxygen. The semiconductor plays the role of catalyst, and is activated in the presence of UV-Vis radiation. Thus, oxidation occurs by positively-charged holes as electron acceptors, generated by exciting an electron, only when the energy provided is higher than the band-gap energy. In addition, the positively-charged hole reacts with water molecules or OH^- to generate strong oxidant OH* radicals.

Photocatalysis is a sustainable alternative to catalytic thermal oxidation, since the latter requires temperatures ranging from 200 °C to 1200 °C, while photocatalysis can occur at room temperature (Shiraishi *et al.* 2009). Compared to other techniques, it is affordable because it involves little maintenance and low power consumption (Shiraishi *et al.* 2009).

In addition to the mineralization of many organic compounds, photocatalysis has also a proven bactericidal effect (Kim *et al.* 2006). The use of photocatalysis has spread rapidly in recent years, and the booming market for indoor air purification products between 2002 and 2003 was attributed to products based on photocatalysis as the operating principle (Paz Y. 2010).

TiO_2 is currently the most widely used catalyst. It is an inexpensive, non-toxic, and biocompatible material that records high photo-efficiency and activity. Other semiconductors such as ZnO, ZnS, CdS, Fe_2O_3, SnO_2 are also commonly used (Mo *et al.* 2009). Studies show that the yields of conversion rates and intermediate by-products vary for different pollutants, being influenced by relative humidity, initial concentration of the compound, recirculating air-flow rate or recycle ratio, residence time, wavelength and intensity of UV radiation, catalyst coating procedure, and its physical form and thickness, among others (Ao *et al.* 2003; Wang *et al.* 2007; Quincy *et al.* 2010).

Quincy *et al.* (2010) have evaluated the effect of residence time, relative humidity and film thickness for pure TiO_2 photocatalysts as key parameters in the design of these types of reaction systems for the degradation of toluene at typical indoor concentrations (10–500 ppbv). These authors have reported toluene removal efficiencies of between 30% and 90%, with higher photodegradation intermediate production under low residence times and moderate humidity conditions. Vildozo *et al.* (2011) have studied photocatalytic oxidation using TiO_2 for treating mixtures of 2-propanol and toluene at concentrations representative of indoor air pollution (80-400 ppbv). In the absence of humidity, the conversion of the two pollutants almost reaches 100%, whereas the conversion of toluene is reduced to 50% in the presence of 60% relative humidity.

Volatile aldehydes are relatively stable by-products of the photocatalytic oxidation of VOCs (Destaillats *et al.* 2012). Ourrad *et al.* (2015) have identified 20 VOC reaction intermediates when limonene photocatalytic oxidation was investigated for an initial concentration of 750 ppbv under dry air conditions. The gas-particle conversion of the reaction intermediates leads to the formation of secondary organic aerosol, which can penetrate deep into the lungs and be easily metabolized.

There are several challenges associated with the use of photocatalysts for indoor air treatment. Most investigations concentrate on contaminant degradation at ppmv levels, while ppbv concentrations have to be measured in indoor air. Other drawbacks are the short lifetime of the catalyst and the generation of harmful by-products.

3.5.7. Cold plasma or non-thermal plasma (NTP)

Plasma is a highly ionized gas produced by high voltage electrical discharges, and generally consisting of electrons, positive ions and neutral particles (atoms or molecules). Regarding the thermodynamic properties of plasma, there are three types: (i) full thermodynamic equilibrium plasma, (ii) located thermodynamic equilibrium plasma, and (iii) any plasma that is not in thermodynamic equilibrium, also called cold plasma or non-thermal plasma. The latter is commonly used for the treatment of indoor air, as it plays a multiple role in air purification. It precipitates particles through electrostatic phenomena, produces UV radiation, and thereby promotes the oxidation of molecules and the removal of viruses and bacteria. Additionally, it also produces free radicals and oxidant species, which promote the breaking of chemical bonds and the transformation of substances such as VOCs into CO_2 and H_2O (Fan *et al.* 2009). Cold plasma can be generated in different ways: pulsed or continuous corona discharge, dielectric barrier discharge, and glow discharge, but it is the continuous corona discharge that is usually used to generate the plasma because it reduces the formation of O_3 during discharge.

Cold plasma requires lower energy requirements compared to thermal plasma, and it is very efficient at removing particulate matter and biological pollution. Liang *et al.* (2012) have applied non-thermal plasma generated by a dielectric barrier discharge to inactivate bacterial and fungal aerosols from the lab-office environment, recording efficiencies of over 95% for bacteria and 85−98% for fungal species.

However, it has several disadvantages, such as poor energy efficiency, especially for the treatment of low VOC concentrations (Vandenbroucke *et al.* 2011). The formation of NO_x and O_3 as a consequence of plasma induction in the NTP reactor is unavoidable. Ozone was generated in the 150–280 ppmv range during the removal of formaldehyde at low concentration (2.2 ± 0.1 ppmv) when using a link tooth wheel-cylinder plasma reactor energized by direct current. Mista and Kacprzyk (2008) have reported the formation of 10 ppmv of NO_x when an air stream containing 70 ppmv was treated, with 93% removal efficiency.

There is a noticeable formation of undesirable by-products that could be more hazardous to a building’s occupants than the treated pollutants. Only 2–4% of methyl-ethyl-ketone converted to carbon dioxide, the remaining carbon being involved in the formation of intermediates, such as methyl nitrate and 2,3-butanedione (Ragazzi *et al.* 2014). The oxidation of toluene and limonene was studied by Hoeben *et al.* (2012), obtaining a conversion of 74% for toluene and 81% for limonene, and generating by-products such as formic acid and carboxylic acids.

Indoor relative humidity has an impact on NTP performance. Electron density and the density of the reactive radicals can be modified by the addition of water vapour, and consequently, the decomposition process may be enhanced or suppressed, depending on the substances involved and the dominant pathway for pollutant destruction. Toluene, n-butane and formaldehyde removal were reported to increase with relative humidity, while the complete degradation of tetrachloromethane, methanol and dimethyl sulfide was adversely affected (Bo *et al.* 2007; Wan *et al.* 2011).

3.5.8. Biofiltration

Biofilters are a cost-effective and eco-friendly alternative to physical-chemical air pollution control methods. This technology can treat a large variety of VOCs and inorganic gases, and the by-products are innocuous (Lu *et al.* 2010). Different bioreactor designs, such as packed bed bioreactor, bioscrubber, biotrickling filter, and membrane bioreactor, have been proposed for the treatment of gaseous pollutants (Kennes *et al.* 2009). However, Guieysse *et al.* (2008) have highlighted the numerous challenges that have to be overcome before this technology can be implemented to tackle indoor pollution (i.e., poor pollutant transfer from gas phase to biofilm, limitations in the case of poorly soluble or recalcitrant substances, and the potential release of dust and microorganisms).

Lu *et al.* (2010) have used a biotrickling filter to treat formaldehyde, benzene, toluene, and xylenes. The removal efficiencies are 100%, 65-70%, 93% and 85-90% for concentrations of 0-6.5 mg/m^3, 2.2-46.7 mg/m^3, 0.5-28.2 mg/m^3 and 4.1-59.0 mg/m^3, respectively. Ondarts *et al.* (2010) have reported the high performance of a packed biofilter treating butanol, butyl-acetate, toluene, limonene, formaldehyde, undecane, and nitrogen dioxide at indoor concentrations ranging from 32 to 140 µg/m^3. The reported efficiency is higher than 90%, and some by-products (acetaldehyde, propanal, acetone, propionic acid, tert-butyl alcohol, ethanol, methanol, and 2-propanol) have been detected at very low concentrations.

3.5.9. Botanical purification

A botanical air purification system is a complementary biofiltration system composed of a vegetable plant and a packing material-substrate. The system passes polluted air through the plant's root system, and uses either the leaves and/or the root bed to adsorb or absorb pollutants from indoor air. Consequently, pollutants become the potential nutrient source for bacterial communities in the soil, and plants enhance the population, diversity and activity of degrading rhizospheric microorganisms by releasing nutrients through their root system. A plant's ability to take up VOCs is well documented in laboratory studies under controlled conditions, but further research on the full capacity of plants and their response in real indoor scenarios is needed.

Yoo *et al.* (2006) have found that toluene and benzene exposure adversely affected the rates of photosynthesis, stomatal conductance and transpiration of four plant species (*Hedera helix L.*, *Spathiphyllum wallisii Regal*, *Syngonium podophyllum Schott.* and *Cissus rhombifolia Vahl.*). Furthermore, each plant's response to a single compound was not necessarily indicative of the response when other compounds were present.

Hanoune *et al.* (2013) and Wang *et al.* (2014) have measured negligible clean air delivery rates (CADR, a parameter often used to quantify the air cleaning ability of portable air cleaners) of around 5–6 m^3 h^{-1} per m^2 bed for static potted plants in indoor rooms (no dynamic air flow through the bed). Hanoune *et al.* (2013) have estimated that several hundreds of *Scindapsus aureus* plants would be required to provide the same CADR as a common ventilation system in an 8 m^3 chamber.

Other studies have found that the microorganisms in the growth medium (rhizosphere) play a major role in the removal of VOCs from the gaseous phase (Wood *et al.* 2002; Orwell *et al.* 2004). In fact, microbial community-shifts were observed when VOC exposure ceased (Russell *et al.* 2014). Kim *et al.* (2014) have concluded that the efficiency of toluene and xylene removal by *Fatsia Japonica* and *Draceana fragans* increased as the root zone volume increased.

Xu *et al.* (2011) have used a dynamic camera to study the removal of formaldehyde by three different plant species (*Chlorphytum comosum*, *Aloe vera* and *Epipremnum* *aureum*). They concluded that formaldehyde assimilation was higher during the day than at night, and that roots played an important role in removing contaminants via adsorption mechanisms and/or enzymatic degradation. Microorganisms were responsible for about 50% of VOC removal during the day, and about 90% at night (Kim *et al.* 2014). Nevertheless, it is worth noting the relevant contribution plants make to aesthetic and mental wellbeing in indoor environments.

3.5.10. Membrane separation

The membrane separation technique relies on the use of a semipermeable membrane that allows the diffusion of certain VOCs from a gas stream to another fluid. Zeolite-based membranes have recently been developed for separating mixtures of gaseous compounds with similar boiling points or molecular weights, mixtures of alcohols, hydrocarbons and non-condensable gaseous compounds. Aguado *et al.* (2004) have shown that membranes based on zeolites are effective for the removal of formaldehyde, n-hexane and benzene, with permeation fluxes of 3300, 130 and 30 mg/m^2h, respectively, and concentrations in the 2-230 ppmv range. The main drawbacks are cleaning requirements, the increase in pressure drop, and greater mechanical resistance during operation.

Nevertheless, the research literature on membrane separation at low VOC levels is limited. Zhang *et al.* (2012) have reported that the material and properties of the polymeric moisture permeable membranes used in air-ventilation heat exchangers significantly reduce the transfer of unwanted pollutants (i.e., acetic acid, formaldehyde, acetaldehyde, toluene, and ethane), as well as the humidity from the exhaust air to the incoming fresh air, back to the indoor environment. They found that polyvinyl alcohol with lithium chloride as an additive, polyvinylpyrrolidone and polyacrylamide membranes were the best choices for use in air-to-air energy exchangers because of their high water vapour permeability and high selectivity. In contrast, polydimethylsiloxane was the least suitable material for this application, followed by polypropylene and ethylene cellulose.

Membrane modules have been installed in manned spacecraft, where a wide range of VOCs has been observed, including aliphatic and aromatic hydrocarbons, alcohols, aldehydes, and chlorinated aliphatic components. In these cases, membranes act as the sorption step, and physically disconnect the contaminated gas phase from a liquid inorganic solution where contaminants are depleted by microbial activity (Van Ras *et al.* 2005). A bench-scale filtration system proved to be effective in the removal of a mixture of indoor VOCs including chlorobenzene, 1,2-dichloroethane, BTEX, alcohols, methane, and acetone in a 20–200 mg m^{-3} range.

3.5.11. Additional features for conventional technologies

The goal of efficiently and safely treating all kinds of indoor pollutants can be elusive. In spite of the wide range of benefits claimed by the manufacturers of air cleaning devices, all these systems have their drawbacks, and further research and development is required.

Although many abatement technologies for improving indoor air quality are frequently selected according to their efficiency in treating a certain set of pollutants, other additional features such as solid waste generation, energy consumption and commercial availability need to be considered (Table 6).

Table 3.6 Qualitative comparison of additional features amongst conventional abatement technologies.

Treatment	Waste generation	Energy consumption	Market sales
Mechanical filtration	Spent filters	Moderate	High
Electronic filtration	Spent cleaning plates	Moderate	High
Adsorption	Spent adsorbent	Moderate	High
Ozonation	---	High	High
Photolysis	Depleted lamps	High	Low
Photocatalysis	Catalyst/lamps	Moderate	Moderate
Non-thermal plasma technology	---	High	Nc[1]
Membrane separation	Clogged membranes/ contaminated solution	High	Nc[1]
Botanical purification	Organic waste	Low	Low
Biofiltration	Biomass and packing material	Low	Nc[1]

[1] Not widely commercialized

As far as the consumer market is concerned, only devices based on adsorption, photocatalysis, ozonation and filtration are widely commercialized today, with filtration being the most popular one (Figure 3.1).

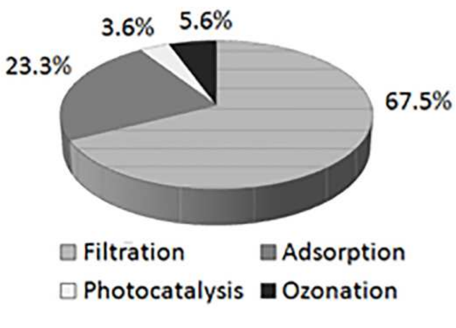


Figure 3.1 The market for devices based on adsorption, filtration, photocatalysis and ozonation for improving indoor air quality (Adapted from Ribot *et al.* 2006)

No single technology can comply with all these requirements simultaneously (Table 6), so many researchers have begun to explore the combination of several air purification technologies or innovative alternatives (Ao and Lee 2005; Delagrange *et al.* 2006; Kwong *et al.* 2008; Lu *et al.*, 2012; Ondarts *et al.*, 2012).

3.6. Combined systems

A universal technology for indoor air treatment has to be able to cope with a wide variety of pollutants at relatively low concentrations, perform effectively at room temperature and humidity, be noiseless and affordable, generate no waste, and consume little energy.

Figure 3.2 shows several combined alternatives that are currently under research, and have not yet been commercialized. The most relevant ones are described below.

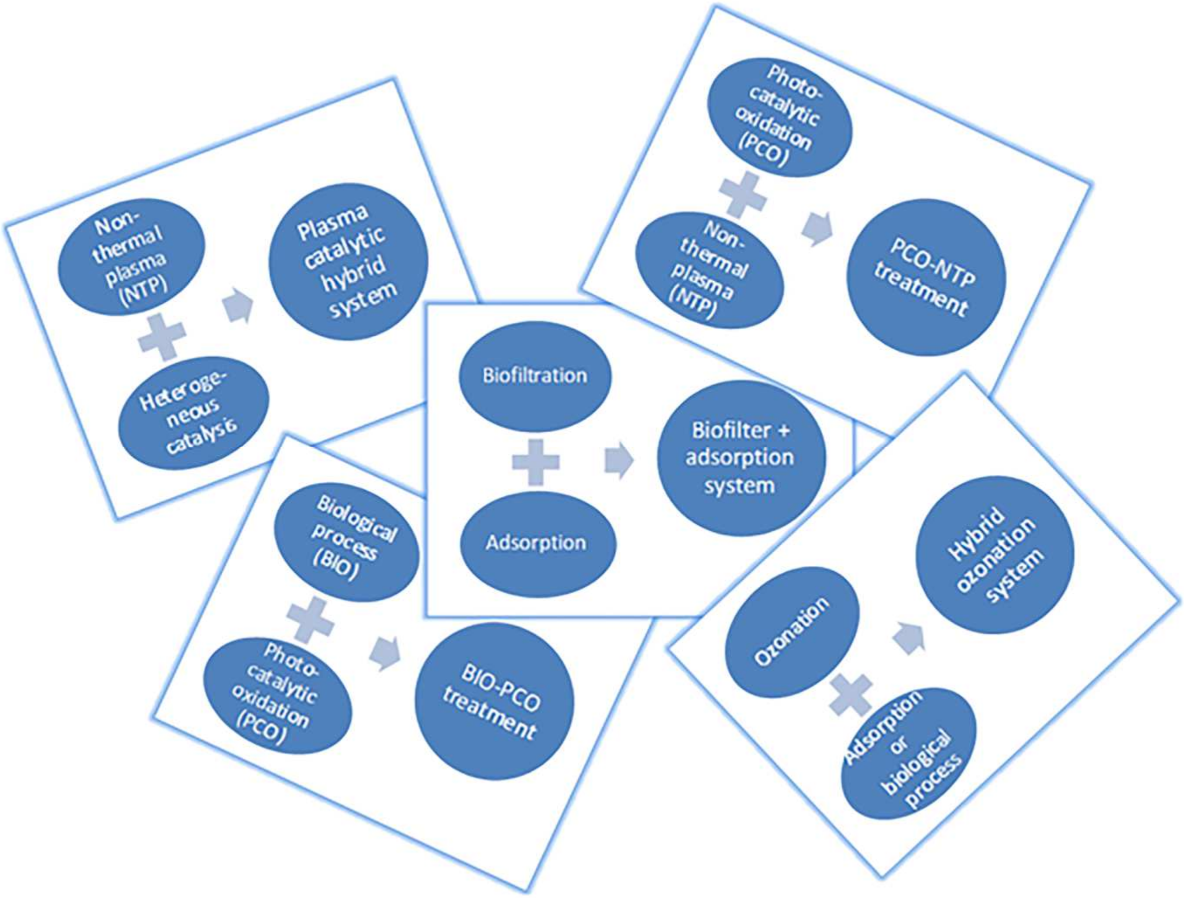


Figure 3.2 Several combined systems under research for the treatment of indoor air

3.6.1. Plasma-catalytic hybrid system

Non-thermal plasma technology (NTP) performs well for the treatment of VOCs, but the generation of toxic by-products during incomplete oxidation has limited its application (Holzer *et al.* 2002). The combination of NTP and a catalyst improves oxidation efficiency, thus avoiding or limiting by-product formation (Delagrange *et al.* 2006). If the catalyst has a significant capacity for adsorbing pollutant molecules, the retention time in the reactor is prolonged, improving the overall removal efficiency (Vandenbroucke *et al.* 2011).

Two reactor configurations have been proposed according to the catalyst position: in-plasma catalysis (IPC), where the catalyst is inside the plasma chamber (Figure 3.3a), or post-plasma catalysis (PPC) where the catalyst is downstream of the discharge zone (Figure 3.3b). Several porous and nonporous materials and metal-coated or bare materials have been used and tested as catalysts in both configurations (i.e., alumina, silica, zeolites, manganese oxides, and TiO_2).

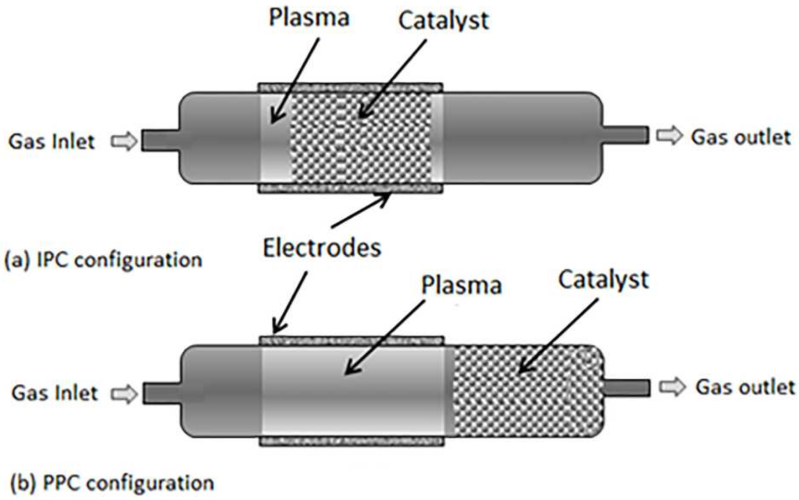


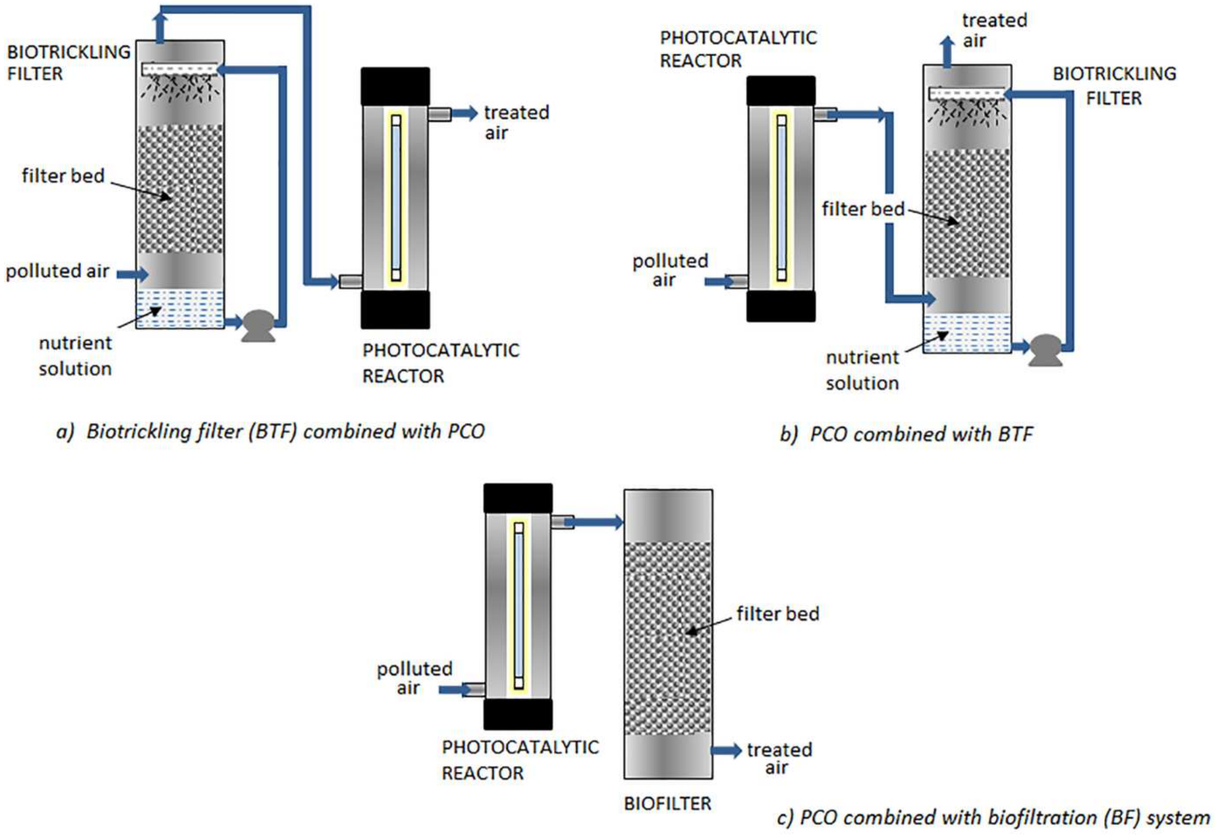
Figure 3.3 Configurations of plasma-catalyst reactor

Fan *et al.* (2009) have compared the results obtained by using NTP and a PPC reactor for the treatment of polluted air containing low concentrations of benzene, toluene and *p*-xylene. The removal efficiency when using NTP technology was 2%, 19% and 49% for benzene, toluene and *p*-xylene, respectively. Nevertheless, treatment by PPC rendered a considerably higher removal efficiency of 94%, 97% and 95%, respectively. Additionally, the emissions of O_3 and NO_2 were considerably reduced.

Van Durme *et al.* (2009) have investigated the effect of relative humidity (RH) on toluene removal in a PPC reactor tested with six different catalysts. Toluene removal efficiency in dry conditions was 90%, but in contrast, when the RH was 72% the removal efficiency decreased to 39%. The effect of catalyst activity and RH content on ozone decomposition rate has been investigated in dry and humid conditions. The physical and chemical properties of the catalysts strongly affect the ozone decomposition efficiencies obtained in the PPC reactor.

3.6.2. Biological process + photocatalytic oxidation hybrid system

Two different biological techniques have been combined with photocatalytic oxidation (PCO) for the treatment of VOCs (Figure 3.4). Thus, PCO can be combined with a biotrickling filter (BTF), with the latter being a pre-oxidation or a post-oxidation step (Figure 3.4a and 3.4b). BTF has the advantage of achieving high efficiency and stability for the treatment of hydrophilic VOCs. Additionally, PCO has a broad selectivity for VOCs, requiring little maintenance and low energy consumption.



a) Biotrickling filter (BTF) combined with PCO

b) PCO combined with BTF

c) PCO combined with biofiltration (BF) system

Figure 3.4 Diagram of biological processes combined with photocatalytic oxidation (PCO)

As far as BTF is concerned, the polluted air stream passes through a column with an inert packing material containing microorganisms. At the same time, a nutrient solution is continuously recycled through the filter bed (Rene *et al.* 2012). Regarding the PCO process, indoor VOCs are decomposed at ambient temperature, but the formation of harmful by-products is a major drawback.

Li *et al.* (2007) have proposed the use of an integrated reactor consisting of a biofiltration unit and a catalytic oxidation unit to treat gaseous waste containing *o*-xylene. The integration of biological and catalytic oxidation processes allows minimizing the biofilter volume, improving the response to shock loads, and leading to high and stable removal efficiency.

He *et al.* (2012) have reported the advantages of using a BTF as a pre-treatment step (Figure 4. a) for the removal of most of the VOCs emitted from paints (ethyl acetate, toluene, ethylbenzene, xylene and trimethylbenzene). Removal efficiencies range from 79.4% to 99.8%. BTF favours high long-term photocatalytic activity by avoiding catalyst deactivation. PCO maintains overall system efficiency when the biological reactor performance is limited or inhibited by specific pollutants and/or load fluctuations and changes in operating conditions.

As a consequence of the bactericidal effect of photooxidation, PCO is able to additionally eliminate possible microorganisms before being released from the biological system (Kim *et al.* 2006). Spore deactivation efficiencies of around 98% have been recorded by Saucedo-Lucero *et al.* (2014) in a fungal perlite-based biofilter coupled with PCO. These authors have contended that direct UV spore inactivation and the formation of oxidative radicals are the main spore inactivation mechanisms.

When using a PCO process before a biological system (Figure 4b and 4c), the prior oxidation of recalcitrant compounds (e.g., trichloroethylene) facilitates subsequent biodegradation. PCO can easily cope with unexpected variations in pollutant inlet concentrations, which cannot easily be overcome in biological systems (Palau *et al.* 2012).

Hinojosa-Reyes *et al.* (2012) have treated ethylbenzene in a combined PCO-Biotrickling filter (BTF) system and in each individual system. Compared to the individual efficiency of the PCO and BTF systems, the hybrid system enhanced the removal efficiency by 47% and 36%, respectively.

3.6.3. Biological process + adsorption hybrid system

Indoor air emissions usually carry fluctuating loads of contaminants throughout the daytime that could hinder the performance of bioreactors due to recurring starvation periods. Several researchers have solved this problem by installing adsorption filters upstream of the biological reactor, which could soften the sudden variations in the concentration, spikes and unstable loads of contaminants (Figure 3.5a). These pre-filters could likewise desorb compounds to reduce the intensity of the starvation periods.

An adsorption column placed after a biofiltration treatment (Figure 3.5b) could restrain the emission of non-biodegrade pollutants and by-products from the bioreactor. Nevertheless, it is worth mentioning that operating failures that entail the loss of biological activity will cause a decrease in the adsorption column lifespan.

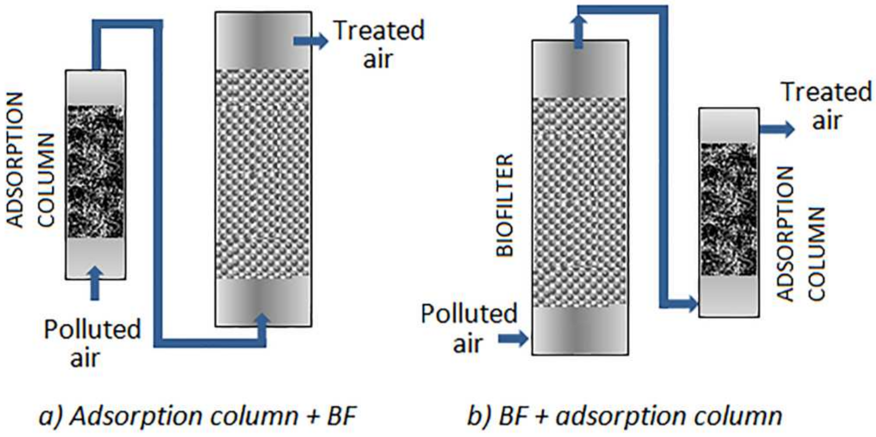


Figure 3.5 Two configurations of the combined biofiltration and adsorption processes

A mixture of a conventional biofilter support and activated carbon may also be used in the same bioreactor, as proposed by Ondarts *et al.* (2012), where, the performance of two biofilters packed with compost and a mixture of compost and activated carbon have been compared for the treatment of eight typical indoor air pollutants. The results show that adding activated carbon to the compost leads to a shorter acclimation period and more stable operation compared with the compost-based biofilter. Moreover, trichloroethylene, which is the only pollutant among the eight tested that is not degraded by biofiltration, is fully adsorbed by the compost/adsorption biofilter.

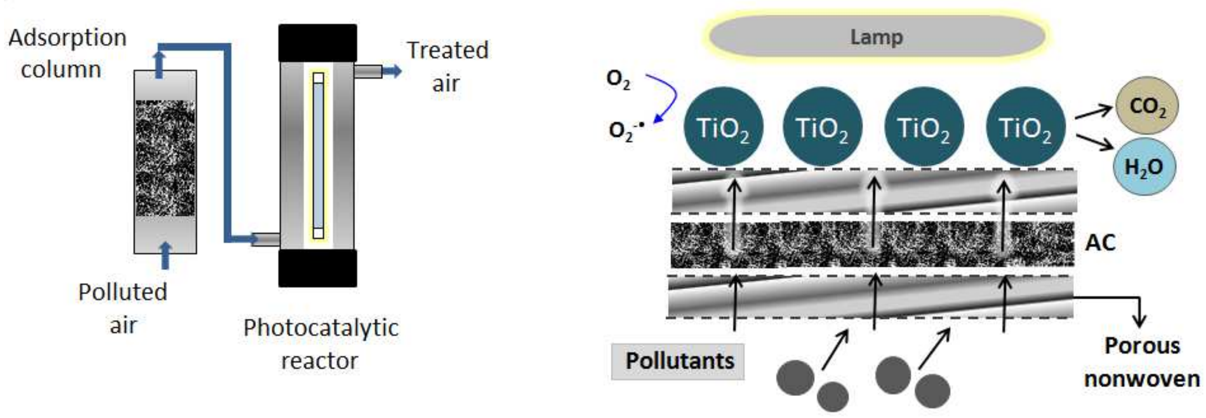
Dorado *et al.* (2012) have reported that high adsorption capacity materials not only play an important role during the start-up operation, but they are also important during steady operation. These authors found that microorganisms were able to oxidize the organic matter previously adsorbed on the surface of activated carbon during starvation periods, and also during steady operation.

3.6.4. Adsorption + photocatalysis hybrid system

The use of an adsorbent before the PCO process (Figure 6) enhances the removal efficiency of indoor pollutants, as the adsorbent retains the pollutant from the gas stream, and partially avoids the early deactivation of the PCO catalyst. As an example, Shiraishi *et al.* (2003) have used a photocatalytic reactor with an adsorption/desorption unit to treat a gas flow containing 0.6 ppmv of formaldehyde. In a further study, Shiraishi *et al.* (2009) have treated toluene in a similar system. They have concluded that if the desorption is carried out at high temperature, a higher amount of toluene is desorbed, and the rate of photocatalytic decomposition increases considerably, although energy consumption significantly increases, too.

A system combining activated carbon (AC) adsorption and photocatalytic oxidation (PCO) has also been tested by Jo and Yang (2009) to treat indoor air levels of BTEX.

This system renders high removal efficiencies (close to 100%), although high desorption temperatures (300 ^{o}C) are required. Ao *et al.* (2003) have sought to improve the photodegradation efficiency of BTEX under high humidity by combining the action of PCO and adsorption. The performance of a TiO_2 filter and a TiO_2/AC filter has been evaluated by Ao and Lee (2005) during the decomposition of toluene at very low concentrations (2.15 ppmv). The authors have concluded that the use of TiO_2/AC not only increases the toluene pollutant removal efficiency (from 50% to 89.5%), but also reduces the amount of intermediate compounds released from the system.



a) System configuration b) Adsorption-photocatalytic process

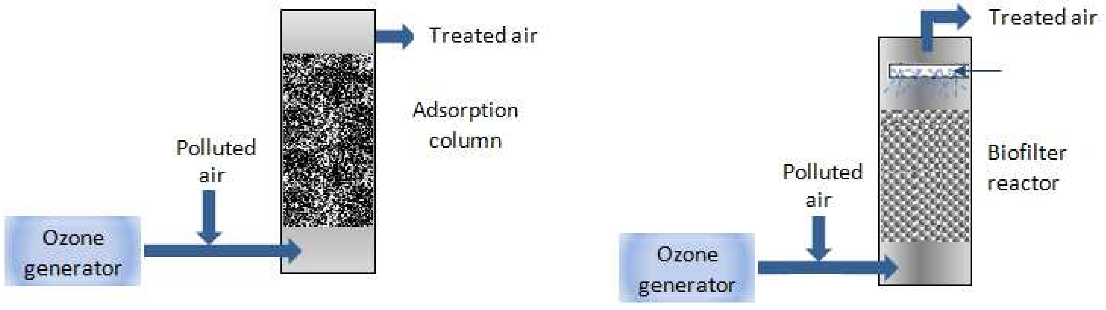
Figure 3.6 Adsorption and photocatalysis hybrid system

3.6.5. Hybrid ozonation systems

Ozonation may be combined with other techniques to potentiate the ozone´s properties (Figure 3.7). Many zeolites or related porous materials may act as a catalyst to accelerate the oxidising activity, and so when ozone is coupled with a suitable adsorbent (Figure 3.7a), the overall conversion efficiency of the catalytic reaction may be increased, even at room temperature, while keeping the residual ozone level low. In addition, energy consumption may be minimized, as frequent regeneration and an intensive energy supply are not required. Kwong *et al.* (2008) have used ozonation with zeolites to remove toluene from indoor air at a concentration of 1.5 ppmv. About 90% of the toluene is removed, and over 98% of the ozone produced is consumed.

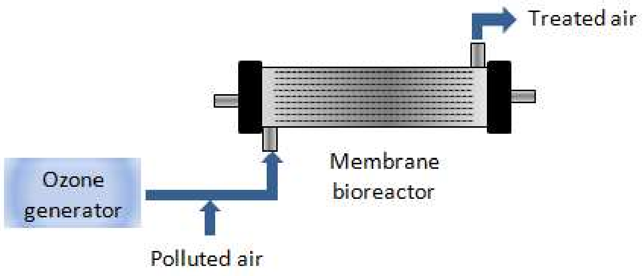
Maldonado-Díaz and Arriaga (2014) have continuously fed ozone into a biofilter (Figure 3.7b), and as a result, they have recorded an improvement in the formaldehyde removal efficiency of up to 98%, as well as longer operating periods. These authors have found that ozone is responsible for effectively maintaining an optimal pH-range in the biofilter between 7.5 and 8.2, due to the carbonate species generated during the reactions between ozone and formaldehyde and its by-products. These authors have also reported that ozone addition decreases the content of exopolymeric substances (EPS) in the biofilm and biofilm thickness without modifying cell viability.

Conversely, Wang *et al.* (2013) have used ozonation before a membrane bioreactor (MBR) previously inoculated with activated sludge to biodegrade xylene (Figure 3.7c). The coupled system has a higher performance and stability for long-term operation than the single MBR system, which is explained by the biomass accumulation control promoted by the ozone. Likewise, Gu *et al.* (2013) have used continuous ozone injections to improve toluene removal efficiency by biofiltration (Figure 3.7b). This configuration has rendered good results in increasing toluene mineralization, in controlling the excessive accumulation of biomass on the packing material and, therefore, in controlling pressure drop increase.



a) Ozone + Adsorption column

b) Ozone + BF



c) Ozone + Membrane bioreactor

Figure 3.7 Different configurations of hybrid ozonation systems

3.7. Conclusions

The number and type of chemical compounds identified and quantified indoors are continuously increasing, and the diversity in their physico-chemical properties makes their joint effective treatment difficult. Amongst commercialized treatment technologies, mechanical filtration is only effective for removing suspended particles, and it generates spent filters that are a new source of contamination. Electronic filtration is also effective for particle removal, although it can generate hazardous charged particles and new pollutants. With regard to adsorption systems, both high relative humidity and pollutant load variations compromise adsorption efficiency. The use of indoor ozone generators as air purifiers does not guarantee the efficient removal of many indoor chemical pollutants, and exposure to high levels of ozone can have a negative impact on occupants´ health. The application of UV photolysis is limited because of its tendency to produce ozone and radicals with harmful effects. Photocatalytic oxidation for indoor air treatment has been applied for contaminant degradation at ppmv levels, while ppbv concentrations have to be measured in indoor air, and their main drawbacks are the short lifetime of the catalyst and the generation of harmful by-products. Cold or non-thermal plasma and membrane separation are other standalone systems that are not yet on the market. Biological treatment systems such as biofiltration and botanical purification are other alternatives under development. In order to overcome many of these drawbacks, several of the aforementioned single technologies have been combined in double-treatment hybrid systems, such as the plasma+catalytic hybrid system, adsorption+photocatalysis hybrid system, and biological process+photocatalytic oxidation hybrid system. In this last proposal, the photocatalytic oxidation system can be combined with a biotrickling filter, with the latter being either a pre-oxidation or a post-oxidation step. These hybrid technologies could be the best option to treat the variety of indoor pollutants. Although further studies of the performance of hybrid technologies in real indoor environments are necessary before developing new devices based on these systems.

References

Aguado S, Polo AC, Bernal MP, Coronas J, Santamaría J. 2004. Removal of pollutants from indoor air using zeolite membranes. Journal of Membrane Science. 240: 159 – 166.

Alberta Health. 2012. Environmental public health indoor air quality manual. A guide for environmental public health professionals. Government of Alberta. http://www.health.alberta.ca/documents/Indoor-Air-Quality-Manual-2012.pdf. Accessed 5 January 2015

ANSES: French Agency for Food, Environmental and Occupational Health & Safety. 2014a. Etude exploratoire du coût socio-économique des polluants de l’air intérieur. Rapport d’étude. http://www.anses.fr/en/documents/AUT-Ra-CoutAirInterieurSHS2014.pdf. Accessed 26 June 2014

ANSES: French Agency for Food, Environmental and Occupational Health & Safety. 2014b. Valeurs guides de qualité d’air intérieur. https://www.anses.fr/fr/content/valeurs-guides-de-qualit%C3%A9-d%E2%80%99air-int%C3%A9rieur-vgai. Accessed 22 December 2014

ANSES: French Agency for Food, Environmental and Occupational Health & Safety (2013). Asbestos: Presentation, health effects, exposure and regulatory framework. https://www.anses.fr/en/content/asbestos Accessed 28 January 2015

Ao CH, Lee SC, Mak CL, Chan LY. 2003. Photodegradation of volatile organic compounds (VOCs) and NO for indoor air purification using TiO2: promotion versus inhibition effect of NO. Applied Catalysis B: Environmental. 42: 119–129

Ao CH, Lee SC. 2005. Indoor air purification by photocatalyst TiO2 immobilizedon an activated carbon filter installedin an air cleaner. Chemical Engineering Science. 60:103 –109

Ayoko GA, Wang H. 2014. Volatile organic compounds in indoor environments. Indoor air pollution, 2nd Edition, Handbook of environmental chemistry. P. Pluschke and H. Schleibinger (eds.) doi:10.1007/698_2014_259

Bacaloni A, Insogna S, Zoccolillo L; 2005. Indoor air quality - volatile organic compounds: sources, sampling and analysis. Chemistry, emission control, radioactive pollution and indoor air quality. Dr. Nicolas Mazzeo (Ed.) doi: 10.5772/21645

Bliss S. 2005. Best Practices Guide to Residential Construction: Materials, Finishes, and Details. John Wiley & Sons.

Bo ZH, Yan JH, Li XD, Chi Y, Cen KF, Chéron BG. 2007. Effects of oxygen and water vapor on volatile organic compounds decomposition using gliding arc gas discharge. Plasma Chemistry and Plasma Processing. 27:546–558

Brauer M, Herderson S, Kirkham T, Lee KS, Rich K, Teschke K. 2002. Review of the health risks associated with Nitrogen Dioxide and Sulfur Dioxide in Indoor Air. Report to Health Canada. University of British Columbia. https://circle.ubc.ca/bitstream/id/3561/IAQNO2SO2full.pdf. Accessed 15 December 2014

Casset A, Braun JJ. 2010. Relationships between indoor allergens, sensitization, and allergic asthma and rhinitis symptoms. Revue des Maladies Respiratoires. 27(8):913-920.

Chen W, Zhang JS, Zhang Z. 2005. Performance of air cleaners for removing multiple volatile organic compounds in indoor air. ASHRAE Transactions. 111(1):1101–1114

Chen JM, Cheng ZW, Jiang YF, Zhang LL. 2010. Direct VUV photodegradation of gaseous α-pinene in a spiral quartz reactor: Intermediates, mechanism, and toxicity/biodegradability assessment. Chemosphere. 81(9):1053–1060

Cheng HH, Hsieh CC, Tsai CH. 2012. Antibacterial and regenerated characteristics of Ag-zeolite for removing bioaerosols in indoor environment. Aerosol and Air Quality Research. 12:409–419

Chithra VS, Shiva-Nagendra SM. 2012. Indoor air quality investigations in a naturally ventilated school building located close to an urban roadway in Chennai, India. Building and Environment. 54:159–167

De Lacy Costello B, Amann A, Al-Kateb H, Flynn C, Filipiak W, Khalid T, Osborne D, Ratcliffe NM. 2014. A review of the volatiles from the healthy human body. Journal of Breath Research. 8;29pp. doi: 10.1088/1752-7155/8/1/014001

Delagrange S, Pinard L, Tatibouët JM. 2006. Combination of a non-thermal plasma and a catalyst for toluene removal from air: Manganese based oxide catalysts. Applied Catalysis B: Environmental. 68:92–98

Destaillats H, Sleiman M, Sullivan DP, Jacquiod C, Sablayrolles J, Molins L. 2012. Key parameters influencing the performance of photocatalytic oxidation (PCO) air purification under realistic indoor conditions. Applied Catalysis B: Environmental. 128:159– 170

Dorado AD, Lafuente J, Gabriel D, Gamisans X. 2012. Interaction between sorption and biodegradation in a biofilter packed with activated carbon. Water Science & Technology. 66(8):1743-1750

Environment Health Standing Committee (enHealth). 2013. Asbestos: A guide for householders and the general public. Australian Health Protection Principal Committee, Canberra
http://www.health.gov.au/internet/publications/publishing.nsf/Content/asbestos-toc. Accessed 12 January 2015

Erdmann CA, Apte MG. 2004. Mucous membrane and lower respiratory building related symptoms in relation to indoor carbon dioxide concentrations in the 100-building BASE dataset. Indoor Air. 14:127–134

Esswein EJ, Boeniger MF. 1994. Effect of an Ozone-Generating Air-Purifying Device on Reducing Concentrations of Formaldehyde in Air. Applied Occupational and Environmental Hygiene. 9(2):139-146

Fan X, Zhu TL, Wang MY, Li XM. 2009. Removal of low-concentration BTX in air using a combined plasma catalysis system. Chemosphere. 75(10):1301-1306

Fisk WJ, Black P, Brunner G. 2011. Benefits and costs of improved IEQ in U.S. offices. Indoor Air. 21:357-67

Fromme H, Nitschke L, Boehmer S, Kiranoglu M, Göen T. 2013. Exposure of German residents to ethylene and propylene glycol ethers in general and after cleaning scenarios. Chemosphere. 90: 2714–2721

Gale RW, Cranor WL, Alvarez DA, Huckins JN, Petty JD. 2009. Semivolatile organic compounds in residential air along the Arizona - Mexico border. Environmental Science and Technology. 43(9):3054-3060

Gallego E, Roca X, Perales JF, Guardino X. 2009. Determining indoor air quality and identifying the origin of odour episodes in indoor environments Journal of Environmental Sciences. 21:333–339

Geiss O, Giannopoulos G, Tirendi S, Barrero-Moreno J, Larsern BR, Kotzias D. 2011. The AIRMEX study - VOC measurements in public buildings and schools/kindergartens in eleven European cities: Statistical analysis of the data. Atmospheric Environment. 45: 3676-3684

Gligorovski S, Weschler CJ. 2013. The Oxidative Capacity of Indoor Atmospheres. Environmental Science and Technology. 47(24):13905-13906

Gu F, Xi J, Hu HY, Tang H. 2013. A new biomass control method by continuous ozone injection in biofilters treating toluene. Proceedings of the 5th IWA Odours and Air Emissions Conference jointly held with 10th Conference on Biofiltration for Air Pollution Control. March 4-7 2013. San Francisco, CA, EU.

Guieysse B, Hort C, Platel V, Munoz R, Ondarts M, Revah S. 2008. Biological treatment of indoor air for VOC removal: Potential and challenges. Biotechnology Advances. 26(5):398-410

Gunschera J, Mentese S, Salthammer T, Andersen JR. 2013. Impact of building materials on indoor formaldehyde levels: Effect of ceiling tiles, mineral fiber insulation and gypsum board. Building and Environment. 64:138-145

Hanoune, B, Nicolas M, Guilhot J, Bulteau G, Cuny MA, Cuny D. 2013. Inefficiency of passive plant-based systems for indoor air cleaning. ASHRAE IAQ 2013 Conference Collection: Environmental Health in Low Energy Buildings. 31–35

He Z, Li J, Chen J, Chen Z, Li G, Sun G, An T. 2012. Treatment of organic waste gas in a paint plant by combined technique of biotrickling filtration with photocatalytic oxidation. Chemical Engineering Journal. 200–202:645-653

Health Canada. 2010. Residential Indoor Air Quality Guideline – Carbon Monoxide. http://www.hc-sc.gc.ca/ewh-semt/pubs/air/carbon_mono/index-eng.php. Accessed 13 December 2014

Health Canada. 2012. Indoor Air Pollutant: Ozone. http://www.hc-sc.gc.ca/ewh-semt/air/in/poll/ozone/index-eng.php. Accessed 29 May 2014

Health Canada. 2014. Residential Indoor Air Quality Guidelines. Canada. http://www.hc-sc.gc.ca/ewh-semt/air/in/res-in/index-eng.php. Accessed 13 December 2014

Hinojosa-Reyes M, Rodríguez-González V, Arriaga S. 2012. Enhancing ethylbenzene vapors degradation in a hybrid system based on photocatalytic oxidation UV/TiO2–In and a biofiltration process. Journal of Hazardous Materials. 209– 210:365– 371

Hoeben WFLM, Beckers FJCM, Pemen AJM, Van Heesch EJM, Kling WL. 2012. Oxidative degradation of toluene and limonene in air by pulsed corona technology. Journal of Physics D: Applied Physics. 45:055202

Holzer F, Roland U, Kopinke FD. 2002. Combination of non-thermal plasma and heterogeneous catalysis for oxidation of volatile organic compounds Part 1. Accessibility of the intra-particle volume. Applied Catalysis B: Environmental. 38: 163–181

Huang Y, Ho SSH, Ho KF, Lee SC, Yu JZ, Louie PKK. 2011. Characteristics and health impacts of VOCs and carbonyls associated with residential cooking activities in Hong Kong. Journal of Hazardous Materials. 186:344-351

Huang ZH, Kang F, Liang KM, Hao J. 2003. Breakthrough of methyethylketona and benzene vapors in activated carbon fiber beds. Journal of Hazardous Materials. B98:107-115

Hubbard HF, Coleman BK, Sarwar G, Corsi RL. 2005. Effects of an ozone-generating air purifier on indoor secondary particles in three residential dwellings. Indoor Air. 15(6):432-444

International Agency for Research on Cancer. 2012. Asbestos (chrysotile, amosite, crocidolite, tremolite, actinolite, and anthophyllite). IARC Monogr Eval Carcinog Risks Hum. 2012;100C:219–309 http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C-11.pdf. Accessed 24 January 2015.

Jiang C, Li S, Zhang P, Wang J. 2013. Pollution level and seasonal variations of carbonyl compounds, aromatic hydrocarbons and TVOC in a furniture mall in Beijing, China. Building and Environment. 69:227-232

Jo WK, Yang CH. 2009. Granular-activated carbon adsorption followed by annular-type photocatalytic system for control of indoor aromatic compounds. Separation and Purification Technology. 66(3):430-442

Kabir E, Kim KH, Ahn JW, Hong OF, Sohn JR. 2010. Barbecue charcoal combustion as a potential source of aromatic volatile organic compounds and carbonyls. Journal of Hazardous Materials. 174:492-499

Kennes C, Montes M, Lopez ME, Veiga MC. 2009. Waste gas treatment in bioreactors: environmental engineering aspects. Canadian Journal of Civil Engineering. 36:1887–1894

Kim JH, Seo G, Cho DL, Choi BC, Kim JB, Park HJ *et al.* 2006. Development of air purification device through application of thin-film photocatalyst. Catalysis Today. 111 (3–4):271–274

Kim KJ, Ahn HG. 2012. The effect of pore structure of zeolite on the adsorption of VOCs and their desorption properties by microwave heating. Microporous and Mesoporous Materials. 152:78-83

Kim KJ, Jung HH, Seo HW, Lee JA, Kays SJ. 2014. Volatile toluene and xylene removal efficiency of foliage plants as affected by top to root zone size. HortSience. 49(2):230–234

Kotzias D, Koistinen K, Kephalopulos S, Schlitt C, Carrer P, Maroni M *et al.* 2005. The INDEX project – Critical appraisal of the setting and implementation of indoor exposure limits in the EU. Report. European Commission. Joint Research Centre, Ispra. 51-74.

Kubba S. 2010. LEED Practices, Certification and Accreditation Handbook. Chapter 7. Indoor Environmental Quality. 211-269

Kwong CW, Chao CYH, Hui KS, Wan MP. 2008. Removal of VOCs from indoor environment by ozonation over different porous materials. Atmospheric Environment. 42:2300-2311

Lan L, Wargocki P, Wyon DP, Lian Z. 2011. Effects of thermal discomfort in an office on perceived air quality, SBS symptoms, physiological responses, and human performance. Indoor Air. 21:376-390

Lee SC, Lam S, Fai HK. 2001. Characterization of VOCs, ozone, and PM10 emissions from office equipment in an environmental chamber. Building and Environment. 36:837–842

Lee CM, Kim YS, Nagajyoti PC, Park W, Kim KY. 2011. Pattern Classification of Volatile Organic Compounds in Various Indoor Environments. Water, Air and Soil Pollution. 215:329-338

Li L, Zhang C, He H, Liu J. 2007. An integrated system of biological and catalytic oxidation for the removal of o-xylene from exhaust. Catalysis Today. 126:338–344

Liang Y, Wu Y, Sun K, Chen Q, Shen F, Zhang J, Yao M, Zhu T, Fang J. 2012. Rapid inactivation of biological species in the air using atmospheric pressure nonthermal plasma. Environmental Sciences and Technology. 46 (6):3360–3368

Liébana EA, Calleja AH. 1998. El aire en interiores: métodos de control y depuración. Enciclopedia de Salud y Seguridad en el Trabajo 45:7-11 www.insht.es/InshtWeb/Contenidos/Documentacion/TextosOnline/EnciclopediaOIT/tomo2/45.pdf. Accessed 22 June 2012

Lin LY, Chen HW, Su TL, Hong GB, Huang LC, Chuang KJ. 2011. The effects of indoor particle exposure on blood pressure and heart rate among young adults: An air filtration-based intervention study. Atmospheric Environment. 45(31):5540-5544

Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT *et al.* 2006. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. Atmospheric Environment. 40:2202-2214

Lu Y, Liu J, Lu B, Jiang A, Wan C. 2010. Study on the removal of indoor VOCs using biotechnology. Journal of Hazardous Materials. 182:204–209

Lu Y, Wang D, Wu Y, Ma C, Zhang X, Yang C. 2012. Synergistic Effect of Nanophotocatalysis and Non thermal Plasma on the Removal of Indoor HCHO. International Journal of Photoenergy. ID 354032

MacIntosh DL, Myatt TA, Ludwig JF, Baker BJ, Suh HH, Spengler JD. 2008. Whole house particle removal and clean air delivery rates for in-duct and portable ventilation systems. Journal of the Air and Waste Management Association. 58:1474–1482

Maldonado-Díaz, G, Arriaga S. 2014. Biofiltration of high formaldehyde loads with ozone additions in long-term operation. Applied Microbiology Biotechnology. doi 10.1007/s00253-014-5848-7

Mallawaarachchi H, De Silva L. 2012. Green framework to improve indoor air quality in buildings: reducing the impact of sick building syndrome on office workers in Sri Lanka: a literature review. International Conference on Sustainable Built Environment. December 14-16 2012, Sri Lanka.

Manéro MH, Monneyron P. 2005. Traitement sélectif de l'air industriel pollué en COV par un procédé hybride adsorption-ozonation. Techniques de l'Ingénieur IN34. http://www.techniques-ingenieur.fr/res/pdf/encyclopedia/42600210-in34.pdf. Accessed 20 June 2012

Mentese S, Rad AY, Arisoy M, Güllü G. 2012. Multiple comparisons of organic, microbial, and fine particulate pollutants in typical indoor environments: Diurnal and seasonal variations. Journal of Air and Waste Management Association. 62:1380–1393

Ministry of the Ecology, Suitable Development, Transport and Accommodation in France. 2011a. Decrees No. 2011-1727 dated the 2nd of December 2011. http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000024909119&dateTexte=&categorieLien=id. Accessed 24 June 2014

Ministry of the Ecology, Suitable Development, Transport and Accommodation in France. 2011b. Decrees No. 2011-1728 dated the 2nd of December 2011. http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000024909128&categorieLien=id. Accessed 24 June 2014

Missia L, Dafni A, Demetriou E, Michael N, Tolis EI, Bartzis JG. 2010. Indoor exposure from building materials: A field study. Atmospheric Environment 44. (35): 4388-4395

Mista W, Kacprzyk R. 2008. Decomposition of toluene using non-thermal plasma reactor at room temperature. Catalysis Today. 137:345–349

Mo J, Zhang Y, Xu Q, Lamson JJ, Zhao R. 2009. Photocatalytic purification of volatile organic compounds in indoor air: A literature review. Atmospheric Environment. 43: 2229-2246

Mølgaard B, Koivisto AJ, Hussein T, Hämeri K. 2014. A new clean air delivery rate test applied to five portable indoor air cleaners. Aerosol Science and Technology. 48:409–417

Moussavi G and Mohseni M. 2007. Using UV pretreatment to enhance biofiltration of mixtures of aromatic VOCs. Jounal of Hazardous Materials. 144:59–66

Nazaroff WW. 2013. Editorial. Four principles for achieving good indoor air quality. Indoor Air. 23:353–356

Ohura T, Amagai T, Senga Y, Fusaya M. 2006. Organic air pollutants inside and outside residences in Shimizu, Japan: levels, sources and risks. Science of the Total Environment. 366:485-99

Ondarts M, Hort C, Platel V, Reguer S, Sochard S, Moynault L. 2010. Developments and new applications of biological gas treatment systems for the removal of micro-pollution in indoor air: study of the design parameters and the associated potential. Proceedings of the 2010 Duke-UAM Conference on biofiltration for Air Pollution Control. 178-187

Ondarts M, Hort C, Sochard S, Platel V, Moynault L, Seby F. 2012. Evaluation of compost and a mixture of compost and activated carbon as biofilter media for the treatment of indoor air pollution. Environmental Technology. 33(3):273-284

Orwell RI, Wood A, Tarran J, Torpy F, Burchett MD. 2004. Removal of benzene by the indoor plant/ substrate microcosm and implications for air quality. Water, Air and Soil Pollution. 157:193–207

OSHA (Occupational Safety and Health Administration). 2012. Sampling and Analytical Methods: Carbon Dioxide in Workplace Atmospheres. http://www.osha.gov/dts/sltc/methods/inorganic/id172/id172.html. Accessed 20 January 2015

Ourrad H, Thevenet F, Gaudion V, Riffault V. 2015. Limonene photocatalytic oxidation at ppbv levels: Assessment of gasphase reaction intermediates and secondary organic aerosolheterogeneous formation. Applied Catalysis B. Environmental. 168–169:183–194

Palau J, Penya-Roja JM, Gabaldon C, Alvarez-Hornos FJ, Martinez-Soria V. 2012. Effect of pre-treatments based on UV photocatalysis and photo-oxidation on toluene biofiltration performance. Journal of Chemical Technolnology and Biotechnology. 87:65–72

Panagiotaras D, Nikolopoulos D, Petraki E, Kottou S, Koulougliotis D, Panayiotis *et al.* 2014. Comprehensive Experience for Indoor Air Quality Assessment: A Review on the Determination of Volatile Organic Compounds (VOCs). Journal of Physical Chemistry & Biophysics. 4:159–171

Paz Y. 2010. Application of TiO2 photocatalysis for air treatment: Patents' overview. Applied Catalysis B: Environmental. 99: 448-460

Pei L, Zhou J, Zhang L. 2013. Preparation and properties of Ag-coated activated carbon nanocomposites for indoor air quality control. Building and Environment. 63:108-113

Quincy N, Vera M, Choi H, Puma G, Dionysiou D, Litter M, Destaillats H. 2010. Effect of key parameters on the photocatalytic oxidation of toluene at low concentrations in air under 254 + 185 nm UV irradiation. Applied Catalysis. B 95:312–319

Ragazzi M, Tosi P, Rada EC, Torretta V, Schiavon M. 2014. Effluents from MBT plants: Plasma techniques for the treatment of VOCs. Waste Management. 34:2400–2406

Rehwagen M, Schlink U, Herbarth O. 2003. Seasonal cycle of VOCs in apartments. Indoor Air. 13:283-291

Rene ER, Veiga MC, Kennes C. 2012. Combined biological and physicochemical waste gas cleaning techniques. Journal of Environmental Science and Health, Part A :Toxic/Hazardous Substances and Environmental Engineering. 47(7):920-939

Ribot B, Frochot D, Blondeau P, Ginestet A, Squinazi F, De Blay F, *et al.* 2006. Mise en place de protocoles de qualification des appareils d'épuration d'air. Convention ADEME-EDF n° 04 04 C 0080. Rapport Final.

Roda C, Barral S, Ravelomanantsoa H, Dusséaux M, Tribout M, Le Moullec Y, *et al.* 2011. Assessment of indoor environment in Paris child day care centers. Environmental Research. 111:1010-1017

Russell JA, Hu Y, Chau L, Pauliushchyk M, Anastopoulos J, Anandan S, Waring MS. 2014. Indoor-biofilter growth and exposure to airborne chemicals drive similar changes in plant root bacterial communities. Applied Environmental Microbiology. 80(16):4805-4813

Sappänen OA, Fisk WJ, Mendell MJ. 1999. Association of ventilation rates and CO2 concentrations with health and other responses in commercial and institutional buildings. Indoor Air. 9:226-252

Sarigiannis DA, Karakitsios SP, Gotti A, Liakos IL, Katsoyiannis A. 2011. Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. Environment International. 37:743–765

Saucedo-Lucero JO, Quijano G, Arriaga S, Muñoz R. 2014. Hexane abatement and spore emission control in a fungal biofilter-photoreactor hybrid unit. Journal of Hazardous Materials. 276: 287–294

Shiraishi F, Yamaguchi S, Ohbuchi Y. 2003. A rapid treatment of formaldehyde in a highly tight room using a photocatalytic reactor combined with a continuous adsorption and desorption apparatus. Chemical Engineering Science. 58:929-934

Shiraishi F, Ishimatsu T. 2009. Toluene removal from indoor air using a miniaturized photocatalytic air purifier including a preceding adsorption/desorption unit. Chemical Engineering Science. 64:2466-2472

Sidheswaran MA, Destaillats H, Sullivan DP, Cohn S, Fisk WJ. 2012. Energy efficient indoor VOC air cleaning with activated carbon fiber (ACF) filters. Building and Environment. 47:357–367

Sittig M. 1991. Handbook of Toxic and Hazardous Chemicals and Carcinogens. 3rd edn. Vol. 2. Park Ridge, New Jersey. Noyes Publications

Srikanth P, Sudharsanam S, Steinberg R. 2008. Bioaerosols in Indoor Environment: Composition, Health Effects and Analysis. Indian Journal of Medical Microbiology. 26:302–312.

Stranger M, Potgieter-Vermaak SS, Van Grieken R. 2007. Comparative overview of indoor air quality in Antwerp, Belgium. Environment International. 33:789–797

Sundell J. 2004. On the history of indoor air quality and health. Indoor Air. 14(7):51-58

Taner S, Pekey B, Pekey H. 2013. Fine particulate matter in the indoor air of barbeque restaurants: Elemental compositions, sources and health risks. Science of The Total Environment. 454–455:79-87

Tseng CC, Li CS. 2005. Inactivation of virus-containing aerosols by ultraviolet germicidal irradiation. Aerosol Science and Technology. 39:1136-1142.

Uhde E, Salthammer T. 2007. Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry. Atmospheric Environment. 41:3111–3128

U.S. Environmental Protection Agency (EPA). 2014. Asbestos Laws and Regulations. http://www2.epa.gov/asbestos/asbestos-laws-and-regulations. Accessed on 20 January 2015

U.S. Environmental Protection Agency (EPA). 2009. Residential Air Cleaners (Second Edition) A Summary of available information. http://www.epa.gov/iaq/pdfs/residential_air_cleaners.pdf Accessed on 13 May 2012

U.S. Environmental Protection Agency (EPA). 1997. Health and Environmental Effects of Ground-Level Ozone. OAQPS Fact Sheet. http://www.epa.gov/groundlevelozone/health.html. Accessed on 24 April 2014

Van Durme J, Dewulf J, Demeestere K, Leys C, Van Langenhove H. 2009. Post-plasma catalytic technology for the removal of toluene from indoor air: Effect of humidity. Applied Catalysis B: Environmental. 87: 78–83

Van Ras N, Krooneman J, Ogink N, Willers H, D'Amico A, di Natale C, *et al.* 2005. Biological air filter for air-quality control. Microgravity applications programme: Successful teaming of science and industry. Edited by Andrew Wilson. p. 270–280

Vandenbroucke AM, Morent R, De Geyter N, Leys C. 2011. Non-thermal plasmas for non-catalytic and catalytic VOC abatement. Journal of Hazardous Materials. 195:30– 54

Vildozo D, Portela R, Ferronato C, Chovelon JM. 2011. Photocatalytic oxidation of 2-propanol/toluene binary mixtures at indoor air concentration levels. Applied Catalysis B: Environmental. 107(3-4):347–354

Wainman T, Weschler CJ, Lioy PJ. 2001. Effects of Surface Type and Relative Humidity on the Production and Concentration of Nitrous Acid in a Model Indoor Environment. Environmental Science Technology. 35:2200-2206

Wang S, Ang HM, Tade MO. 2007. Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. Environment International. 33:694-705

Wang C, Xi JY, Hu HY, Yao Y. 2009. Advantages of combined UV photodegradation and biofiltration processes to treat gaseous chlorobenzene. Journal of Hazardous Materials. 171:1120–1125

Wan Y, Fan X, Zhu T. 2011. Removal of low-concentration formaldehyde in air by DC corona discharge plasma. Chemical Engineering Journal. 171:314–319

Wang Z, Xiu G, Qiao T, Zhao K, Zhang D. 2013. Coupling ozone and hollow fibers membrane bioreactor for enhanced treatment of gaseous xylene mixture. Bioresources Technology. 130:52–58

Wang Z, Pei J, Zhang JS. 2014. Experimental investigation of the formaldehyde removal mechanismsin a dynamic botanical filtration system for indoor air purification. Journal of Hazardous Materials. 280:235–243

Waring MS, Siegel JA. 2011. The effect of an ion generator on indoor air quality in a residential room. Indoor Air. 21:267–276

Weichenthal S, Dufresne A, Infante-Rivard C. 2007. Indoor ultrafine particles and childhood asthma exploring a potential public health concern. Indoor Air. 17(2):81–91.

Weschler CJ. 2009. Changes in indoor pollutants since the 1950s. Athmospheric Environment. 43:153-169

Weschler CJ. 2000. Ozone in Indoor Environments: Concentration and Chemistry. Indoor Air. 10:269-288

Wood A, Orwell RL, Tarran J, Torpy F, Burchett M. 2002. Potted-plant/growth media interactions and capacities for removal of volatiles from indoor air. Journal of Horticulture Science Biotechnology. 77(1):120–129

World Health Organization (WHO). 1989. Indoor Air Quality: organic pollutants. Report WHO Meeting, Berlin, 23-27 August 1987. EURO Reports and Studies 111. Regional Office for Europe, Copenhagen.

World Health Organization (WHO). 2000. Air Quality Guidelines for Europe (2nd Edition). World Health Organization Regional Publications, European Series No. 91. Health Organization, Regional Office for Europe, Copenhagen. http://www.euro.who.int/document/e71922.pdf. Accessed July 2012

World Health Organization (WHO). 2010. WHO Guidelines for Indoor Air Quality: Selected pollutants. World Health Organization Regional Office for Europe, Copenhagen. http://www.euro.who.int/document/e71922.pdf. Accessed 22 May 2014

World Health Organization (WHO). 2013. Asthma. Media Center. Fact sheet N°30 2013. http://www.who.int/mediacentre/factsheets/fs307/en/. Accessed 22 May 2014

World Health Organization (WHO). 2014. Public Health, Environmental and Social Determinants of Health (PHE). Geneva. http://www.who.int/phe/health_topics/outdoorair/databases. Accessed 25 June 2014

Xu Z, Wang L, Hou H. 2011. Formaldehyde removal by potted plant-soil systems. Journal of Hazardous Materials. 192: 314-318

Yoo MH, Kwon YJ, Son KC, Kays SJ. 2006. Efficacy of indoor plants for the removal of single and mixed volatile organic pollutants and physiological effects of the volatiles on the plants. Journal of the American Society for Horticultural Science. 131(4):452–458

Yu BF, Hu ZB, Liu M, Yang HL, Kong QX, Liu YH. 2009. Review of research on air-conditioning systems and indoor air quality control for human health. International Journal of Refrigeration. 32:3-20

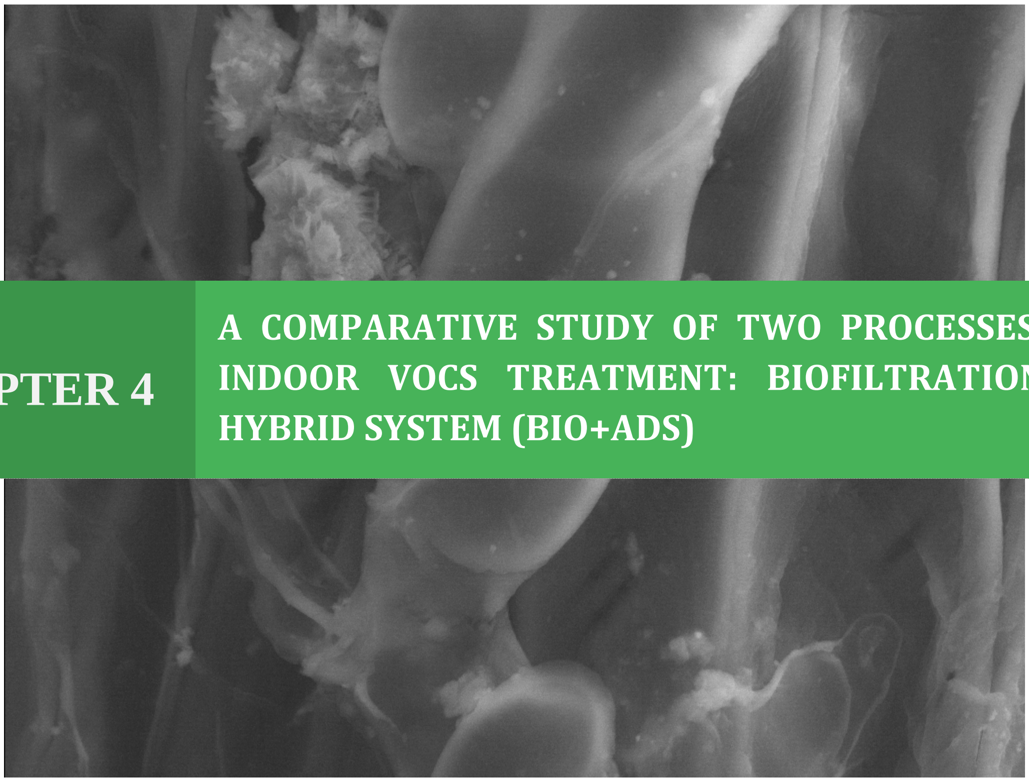
Zaatari M, Nirlo E, Jareemit D, Crain N, Srebric J, Siegel J. 2014. Ventilation and indoor air quality in retail stores: A critical review (RP-1596). HVAC&R Research. 20:276–294

Zhang Y, Moa J, Li Y, Sundell J, Wargocki P, Zhang J, *et al.* 2011. Can commonly-used fan-driven air cleaning technologies improve indoor air quality? A literature review. Atmospheric Environment. 45:4329-4343

Zhang LZ, Zhang XR, Miao QZ, Pei LX. 2012. Selective permeation of moisture and VOCs through polymer membranes used in total heat exchangers for indoor air ventilation. Indoor Air. 22:321–330

Zhao P, Siegel JA, Corsi RL. 2007. Ozone removal by HVAC filters. Atmospheric Environment. 41 (15): 3151–3160

Zhao W, Yang Y, Dai J, Liu F, Wang Y. 2013. VUV photolysis of naphthalene in indoor air: Intermediates, pathways, and health risk. Chemosphere. 91:1002–100.



CHAPTER 4

A COMPARATIVE STUDY OF TWO PROCESSES FOR INDOOR VOCS TREATMENT: BIOFILTRATION VS. HYBRID SYSTEM (BIO+ADS)

4. A COMPARATIVE STUDY OF TWO PROCESSES FOR INDOOR VOCs TREATMENT: BIOFILTRATION VS. HYBRID SYSTEM (BIOLOGICAL PROCESS+ADSORPTION).

4.1. Introduction

4.1.1. Context

There are hundreds of organic chemicals in indoor air, but most are present in very low concentrations (<50 µg m^{-3}) (Wechler, 1990; Kostiainen, 1995; Geiss *et al.*, 2011). The organic compounds are the major contributors to the deterioration of Indoor Air Quality (IAQ). Within this group, the most representative are the volatile organic compounds (VOCs) which are part of different chemical families and have multiple sources (see Table 4.1). Other significant pollutants are the semi-volatile organic compounds (SVOCs) which include phthalates, brominated/organophosphate flame retardants and polycyclic aromatic hydrocarbons (PAH) (Destaillats *et al.* 2008). The PAHs include the benzo[a]pyrene which is classified as a human carcinogen (Romagnoli *et al.*, 2014).

Table 4.1 Potential sources of VOCs in indoor environments (Jones, 1999; Wang *et al.*, 2007; Salthammer, 2009; Schlink *et al.*, 2010).

Family	Potential sources
Acetate/ aldehydes	Pressed wood products, particleboard, new books and magazines, paintings, cigarette smoke, insulation, photocopiers, carpets, furnishings, algaecides and combustion in vehicles.
Aromatic Hydrocarbons	Combustion, paintings, cigarette smoke, glues, fuels, plastic, photocopiers, fuels, varnishes, insulation materials, products for weatherisation , cigarette smoke, inks, carpets and insecticides.
Aliphatic hydrocarbons	Combustion, wood stains, glues for floor waxes, paints, cleaning products for floors, carpets and upholstery and plasterboard.
Esters and glycol esters	PVC, plastic / melamine lacquers, paints (latex) paints, soaps, cosmetics, fungicides, herbicides, for the treatment of wood.
Chloride hydrocarbons	Paints, varnishes, adhesives, metal cleaners, dry cleaning, carpets, rugs, anti-mite, deodorant, wood paneling.
Terpenes	Air fresheners, deodorants, cleaning floors, furniture polishes, fabrics, fabric softeners
Alcohols	Manufacture of plastics, coating materials, adhesives, printing inks, and impregnating agents, flavoring food and drink, cosmetics and adhesives

The severity and nature of the contaminants' health effects depend on many factors including the level and duration of exposure. Currently, there is little information about the health effects of organic pollutants exposure in closed environments; however, studies reported symptoms that include eyes, nose and throat irritation, headaches, allergic skin reactions, dyspnea, nausea, nosebleeds, fatigue, dizziness (Colman Lerner *et al.*, 2012).

The Joint Research Centre of the European Commission carried out the project "Critical Appraisal of the Setting and Implementation of Indoor Exposure Limits in the EU" from December 2002 to December 2004 (Kotzias *et al.*, 2005). This study included a risk assessment process which prioritized 14 compounds that were found to have the highest health risk in European population. A ranking was arranged with the 14 chemicals assigned to three groups: high priority chemicals (formaldehyde, benzene, carbon monoxide, nitrogen dioxide and naphthalene); second priority chemicals (acetaldehyde, toluene, meta, para and ortho xylene and styrene) and chemicals requiring further research with regard to human exposure or dose response (ammonia, d-limonene and α-pinene).

On the other hand, the Observatory of Indoor Air Quality (OQAI), created by French authorities, deals with a permanent data collection system of indoor pollutants measured in different environments such as dwellings, school facilities, public buildings, work and leisure places. The OQAI carried out a survey between 2003 and 2005; chemical, biological and physical parameters were identified and quantified indoors. The survey reveals aldehydes (formaldehyde, acetaldehyde and hexaldehyde) as the most frequent and most concentrated gas in dwellings and toluene and m/p-xylene as the most frequent aromatic hydrocarbons in such places (Kirchner *et al.*, 2006).

Figure 4.1 presents a compilation of VOCs reported by two studies: VOCs average concentration is taken from measurements done in the frame of the AIRMEX project (Geiss *et al.*, 2011) and from the national campaign conducted by the OQAI between the years 2003-2005 to determine the status of IAQ in French dwellings (Kirchner *et al.*, 2006). Thirteen of the 27 reported compounds were common to both studies and the order of magnitude of the mean concentration was similar between them except for compounds n-decane and hexaldhehyde. Four compounds reported in the project AIRMEX draw attention by its high average values: α-pinene, α-limonene, 1-butoxy-2-propanol and acetone. The α-pinene and d-limonene are widely used in cleaning products. Tetrachloroethylene and trichlorethylene are part of the six substances identified as priorities by the OQAI and for which guideline values have been published; they have been considered as possible carcinogens.

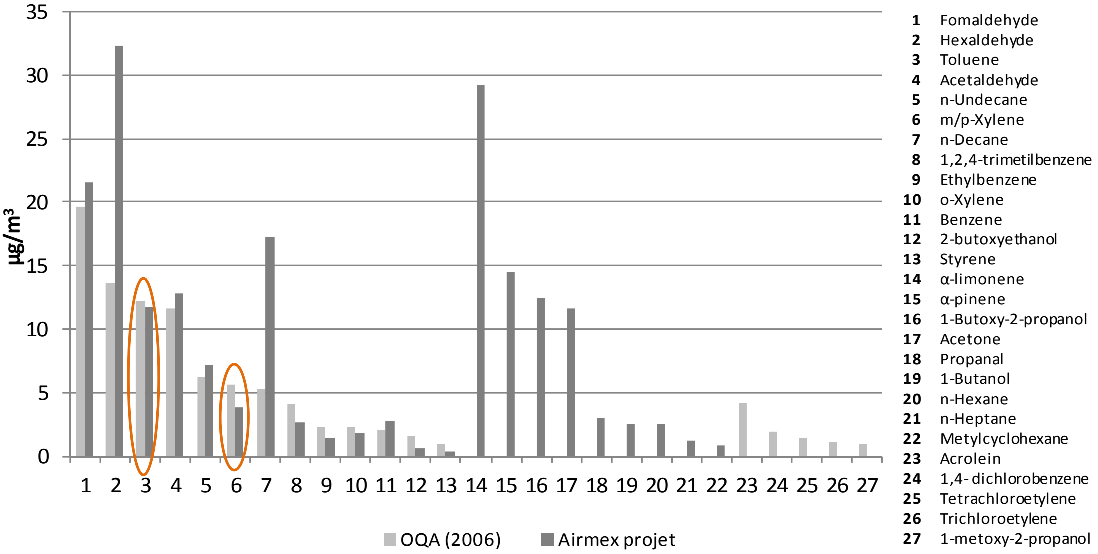


Figure 4.1 VOCs commonly found in indoor air of homes (Geiss *et al.* 2011; Kirchner *et al.*, 2006).

Special strategies for improving IAQ have been studied not only for reducing health effects but also as a way to improve workers' performance (Wargocki, 2011; Seppanen and Fisk, 2006). These strategies include new policies regarding building materials, ventilation rate in working places, development of lower-emission products, regulation of environment temperature and moisture, rational use of chemical products (insecticides, air fresheners, cleaning products, scented candles, etc.) indoors. Nevertheless, most of these strategies are recent and have not been extensively implemented yet.

The treatments of chemical indoor air pollution, previously presented in Chapter 3, include hybrid systems, from those biofiltration and adsorption will be used in this study.

4.1.2. Scope of the study

The overall objective of this chapter is to compare biofiltration technology and a hybrid system (biofiltration coupled to adsorption onto activated carbon) as possible methods to treat indoor air pollution.

First of all, an organic material (ABONLIR^{TM}) supplied by the Spanish company SLIR (Specialised Engineering in Recycling Agricultural Residues) was chosen as packing material for biofiltration stage considering its good performance in similar studies conducted by the Biofiltration Research Group at the Engineering Faculty in Bilbao (University of the Basque Country, UPV/EHU). In this part of the study, material acclimation was carried out at higher concentrations (ppm levels) than those normally found in indoor environments (ppb levels) which could represent concentration peaks associated to specific indoor activities such as cooking and cleaning.

Empty Bed Residence Time (EBRT) is an essential parameter in reactors' design. A specific study considering low EBRTs (2.5-23 s) in biofiltration was carried out at ppb level concentrations. Another objective of this study is to prove that even at low concentrations (µg m^{-3}), biofiltration is able to achieve high removal efficiencies (>80%) for the target pollutants. Nevertheless, due to heterogeneity of indoor pollutants, the combination of different technologies turns out to be necessary. In this context, biofiltration (BF) and the hybrid system (HS) were implemented and their performances (at ppb levels) were compared.

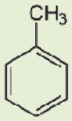
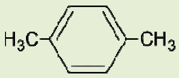
4.1.3. Target pollutants

In order to study the removal of indoor VOCs, toluene and p-xylene were selected as target compounds because of their frequency in indoor environments (see Figure 4.1) and because they are widely studied in the research area of air treatment and can therefore be used to compare the performance of different systems.

4.1.3.1. Physic-chemical properties

Physical and chemical properties of the target pollutants (toluene and p-xylene) are reported in Table 4.2.

Table 4.2. Physicochemical properties of toluene and p-xylene.

Parameter	**Value**	
	Toluene 	p-Xylene 
Molar weigh (g mol^{-1})	92.13	106.17
Boiling point (°C)	110.6	138.5
Vapour pressure (Pa)	2922 (20 °C) 3769 (25 °C)	863 (20 °C) 1172 (25 °C)
Solubility (mg L^{-1})	515 (20 °C)	177 (25 °C)
Air diffusion coefficient (cm^2 s^{-1})	8.7x10^{-2} (25 °C)	7.2x10^{-2} (25 °C)
Henry constant (at 24.63 °C)[a]	0.228	0.268

(a) Henry constant was calculated at the average temperature of the experimental trials (24.63 °C) following the equation presented by Staudinger and Roberts (2001).

4.1.3.2. Sources

Toluene is released in indoors from numerous sources: cleaning products, stains, paints, paint strippers and thinners, shellac, fingernail polish, lacquers, adhesives, rubber and protective coatings contain toluene (WHO, 1989). Other sources include wood office furniture, vinyl flooring and vehicle emissions (toluene is used in gasoline to enhance the octane ratings) (Sarigiannis, 2011). Typical indoor concentrations in Europe range from 1 µg m^{-3} to 160 µg m^{-3} (0.27-42.5 ppb) in public buildings and dwellings (Geiss *et al.*, 2011).

Xylene exists in three isomeric forms: ortho-, meta- and para-xylene. It is widely used as a solvent in printing, rubber, paint and leather industries (Kandyala *et al.*, 2010). Tobacco smoke and pesticide formulations are also a source of xylenes in indoors (Sarigiannis, 2011; Kotzias, 2005). Typical European indoor concentrations for xylenes range from 0.5 µg m^{-3} to 75.1 µg m^{-3} ($8.8x10^{-2}$-13,27 ppb) in public buildings and dwellings (Geiss *et al.*, 2011).

4.1.3.3. Health effects

Toluene

Toluene can enter the human body by inhalation and/or ingestion. Short-term exposure may cause irritation of the skin, eyes and respiratory tract. The central nervous system (CNS) is also affected by short-term exposure to high levels of toluene resulting in light-headedness, euphoria, dizziness, sleepiness, unconsciousness, headaches and nausea. Long-term exposures also cause irritation of the respiratory tract, eyes and skin, sore throat, dizziness, and headaches. At high concentrations, CNS depression can be presented including symptoms such as tremors, loss of muscle control and problems with speech, vision, and hearing (ANSES, 2011; Australian Government, 2014a; U.S. EPA, 2005). Standards and guidelines established by the American National Institute for Occupational Safety and Health (NIOSH), the American Occupational Safety and Health Administration (OSHA) and the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) are:

-OSHA PEL (permissible exposure limit) = 200 ppm in average over 8 h

- NIOSH IDLH (immediately dangerous to life or health) = 500 ppm

-ANSES VTR (reference toxicological value by continuous inhalation) = 0.8 ppm (to avoid neurological adverse effects)

Xylene

Xylenes (individual of mixed isomers) may irritate the eyes, nose and throat. Short-term exposure to high levels of xylene can also cause difficulty in breathing; impaired function of the lungs and neurological effects. Long-term exposure to high concentrations of xylene affects the nervous system, causing headaches, tremors, dizziness, confusion, and changes in one's sense of balance; respiratory, cardiovascular, and kidney effects have also been reported. (Australian Government, 2014b; US EPA, 1999). Standards and guidelines established by the American National Institute for Occupational Safety and Health (NIOSH) and the American Occupational Safety and Health Administration (OSHA) are:

- OSHA PEL (permissible exposure limit) = 100 ppm in average over 8 h
- NIOSH IDLH (immediately dangerous to life or health) = 895 ppm
- NIOSH STEL (short term exposure level limits to 15 min) = 150 ppm

4.1.4. Biodegradation process: Biofilter (BF)

Nowadays, biofiltration is a competitive technology for the VOCs treatment because of its simple operation, low operating and maintenance costs (Rojo *et al.*, 2011) and its ability to cope with moderately hydrophobic pollutants (Estrada *et al.* 2011).

4.1.4.1. Principles

A complex combination of physicochemical and biological phenomena takes place during the elimination of pollutants in a biofilter (Figure 4.2). First of all, a mass transfer of pollutants and oxygen occurs from the gas phase to the aqueous phase (biofilm). It is also possible that pollutants are absorbed by the packing material (Devinny and Ramesh, 2005). Then, microorganisms contained in the biofilm degrade inside their cells the pollutants following the exothermic reaction:

$$\text{Pollutant} + O_2 \xrightarrow[\text{nutrients (N, P, K, trace-elements)}]{\text{microorganisms}} H_2O + CO_2 + \text{biomass} \quad (\Delta H < 0)$$ Equation 4.1

Water and carbon dioxide resulting from the oxidation reaction are transferred to the gas phase. Organic packing material provides water, carbon and nutrients and serves as a support to the biofilm (Deshusses, 1997).

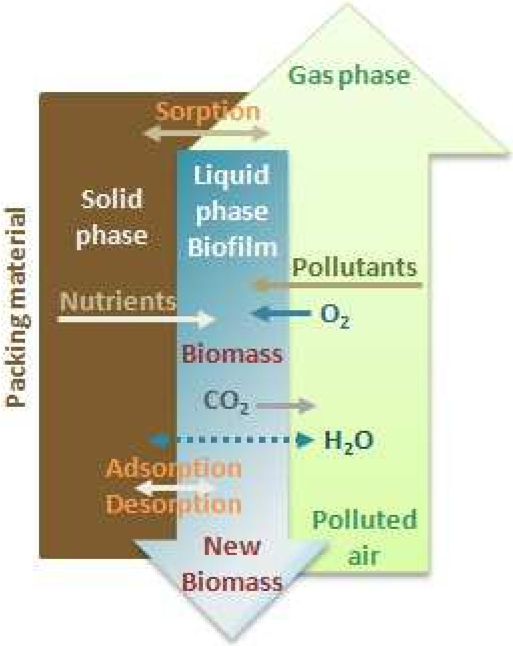


Figure 4.2 Degradation principles in biofilters (Adapted from Deshusses, 1997)

4.1.4.2. Biofilter operating parameters

The following parameters are important for the interpretation of results and comparison among other systems or to scale up for industrial applications. Table 4.3 shows the variables involved in biofiltration performance:

Table 4.3. Biofilter operating parameters.

Parameter	Description	Equation	Units
EBRT (Empty bed residence time)	Time the polluted air spends in the reactor, considering that the reactor is empty.	$EBRT = \frac{V_r}{Q}$	h
τ (true residence time)	Time the polluted air spend in the reactor, including the porosity of the packing.	$\tau = \frac{V_r * \varepsilon}{Q}$	h
IL (inlet load)	Quantity of pollutant that enters the biofilter per volume and per time.	$IL = \frac{C_{in} * Q}{V_r}$	g $m^{-3}h^{-1}$
EC (elimination capacity)	Mass of contaminant degraded per volume and per time.	$EC = \frac{(C_{in} - C_{out}) * Q}{V_r}$ $EC = IL * RE/100$	g $m^{-3}h^{-1}$
RE (removal efficiency)	Fraction of contaminant removed by biofilter.	$RE = \frac{C_{in} - C_{out}}{C_{in}} * 100$	%

Variables involved
V_r : reactor volume (m^3)
Q : Inlet air flow (m^3 h^{-1})
ε : Porosity of the packing material
C_{in} : Biofilter inlet concentration (g m^{-3})
C_{out} : Biofilter outlet concentration (g m^{-3})

Other parameters should be continuously monitored to evaluate the general operation of the system over time: temperature, relative humidity, pressure drop, media properties, moisture, pH and nutrient availability.

4.1.4.3. Properties of the packing material

Packing material significantly influences biofilters operation and performance. Most relevant properties are presented in Table 4.4.

Table 4.4. Relevant characteristics of a good packing material.

Parameter	Influence over biofiltration and specific requeriments	Values	References
Presence of indigenous microorganisms	Suitable in order to avoid inoculation step and to reduce acclimation time		Devinny *et al.*, 1999
Specific surface area	Large for biomass attachment and pollutant mass transfer.	300-1000 m^2 m^{-3}	Dumont and Andres, 2010; Herrygers *et al.*, 2000
Bulk density	Low to avoid bed compaction and less demanding reactor vessel.		Gaudin *et al.*, 2008
Sorption characteristics	Sufficient to attenuate concentration peaks and high		Devinny *et al.*, 1999 Dumont *et al.*, 2008

Parameter	**Influence over biofiltration and specific requeriments**	**Values**	**References**
	buffering capacity to avoid large pH fluctuations.		
Moisture content	Large amounts of water are necessary to favour microbial development.	20-60%	Gaudin *et al.*, 2008
Void fraction	Exhibition of a high porosity to reduce the pressure drop across the bed**.**	0.4 to 0.9	Devinny *et al.*, 1999
Structural stability	Structure should remain stable with time to avoid clogging or shrinking and to increase the biofilter lifespan.		Devinny *et al.*, 1999; Estrada *et al.*, 2011
Suitable growth environment	Presence of nutrients in order to maintain microbial activity. Alternative carbon source.		Devinny *et al.*, 1999
Cost	Low because of its large contribution to the overall operating costs.		Estrada *et al.*, 2012.
Disposal	It should be easily and cheaply disposable.		Devinny *et al.*, 1999

4.1.5. Hybrid system (HS)

Process intensification can be defined as a strategy to get compact, energy-efficient, safe and environmentally friendly processes. Our strategy deals with using biofiltration coupled with adsorption onto activated carbon to get higher removal efficiencies compared to those obtaining only by biofiltration. As can be seen in Figure 4.3, the idea is to use a column of activated carbon after the biofilter in order to eliminate compounds hardly biodegraded and by-products of the biofiltration stage (see section 3.6.3). In fact, biofiltration is very sensitive to load fluctuations, does not treat non-biodegradable compounds, might emit bio-by-products and require a large area for its installation. These limitations could be overcome by coupling this technique with other process such as adsorption technology which offers a good response in the case of load fluctuations can treat several indoor contaminants and does not have significant space requirements. The biofiltration principle was described in the previous section (see 4.1.4).

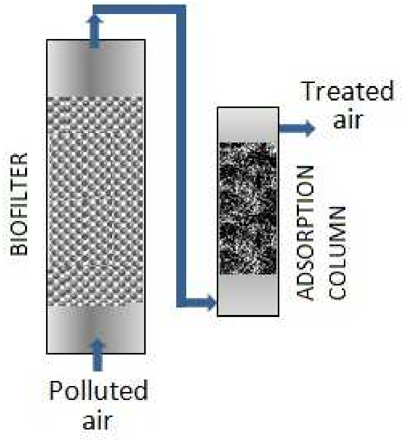


Figure 4.3 Hybrid system schematization.

The adsorption is the process by which certain molecules of a fluid (gas or liquid), called adsorbate, are fixed on the surface of a solid, the adsorbent. The adsorption process is an exothermic process and is based on the selective adsorption of different substances by specific interactions between the surface (external and internal) of the adsorbent and the adsorbed molecules. These interactions lead to two types of adsorption: physical adsorption and chemical adsorption. In the first, the adsorbate molecules will fix on the surface of the adsorbent through Van der Waals forces. Chemical reactions are involved in the second one. In physical adsorption, there is no molecular structure modification of the adsorbent so that it is a perfectly reversible process; the molecules can be desorbed by decreasing the pressure, increasing temperature or by using a warm gas through the AC bed (air, water vapour, inert gas). In the case of chemical adsorption, energy of bonds formed is much stronger and therefore the process is less reversible and could even become irreversible (Meunier & Sun, 2003). The adsorption capacity of an adsorbent can be established through adsorption isotherms determined at a given temperature (Garcia & Perez, 2003).

The adsorption has been successfully applied in controlling emissions of VOCs at industrial level. Its adaptation to indoor air treatment has been the subject of numerous studies (Yao *et al.*, 2009; Sidheswaran *et al.*, 2012; Jo and Yang, 2009; Cheng *et al.*, 2012). Volatile organic compounds (VOCs) and other pollutants present in indoor environments can be retained on the surface of an adsorbent material such as activated carbon (AC), zeolites, silica gel, activated alumina, mineral clay and certain polymers (Yang, 2003). Those materials have an important specific surface area and therefore will retain high quantity of pollutants on their surface. Nevertheless, they are not able to remove all the pollutants as they are developed to remove specific pollutants as can be seen in Table 4.5. Furthermore, Estrada's research shows that adsorption onto AC had the highest operating costs compared to other technologies evaluated in his research (Estrada el al., 2011). Those operating costs were associated to the short lifespan of the AC, the necessity of regeneration and the disposal as hazardous waste.

However, activated carbon is extensively used in purification of indoor air due to the low concentration levels to be treated. With a large specific area and a high adsorption capacity, the AC will have a longer lifespan in indoor environments than in industrial ones.

Table 4.5. Properties of adsorbent materials.

Adsorbent	**Specific surface area (m^2 g^{-1})**	**Pore size (nm)**	**Internal porosity**	**Bulk density (kg m^{-3})**	**Target pollutants**
Activated carbon-AC (1)	400-2000	1.0-4.0	0.4-0.8	300-600	Organic and inorganic compounds
Zeolites (2)	500-800	0.3-1.0	0.3-0.4	600-750	NOx, COVs
Sílica gel (1)	300-800	2.0-14.0	0.4-0.5	700-800	Amines, aromatics and H_2O
Activated alumina (3)	200-400	1.0-6.0	0.3-0.6	800-950	Odours, H_2O
Polymers (2)	100-700	4.0-25	0.4-0.6	400-700	COV

(1) Le Cloirec, 2003; (2) Buekens A. and Zyaykina N.N., 2009; (3) Knaebel, 2004.

4.2. Materials and methods

This study was carried out in two different steps. The first part was developed in the Biofiltration research group at the Engineering Faculty in Bilbao (University of the Basque Country, UPV/EHU) and consisted in discovering the principles of biofiltration technology, choosing the packing material for biofilters and studying its performance at ppm concentration levels. Material inoculation and acclimation was accomplished in this part of the study. This acclimated material was used for biofiltration steps of the second part of the study. The second part of the study took place in the Laboratory of Thermal, Energy and Processes of the University of Pau at the Tarbes site. EBRT, drying studies, and design approach were carried out. Additionally, the implementation of a biofilter (BF) and a hybrid system (HS) to treat a mixture of toluene and p-xylene at ppb concentration levels also took place in this laboratory. Experimental set-ups and operating conditions for all the laboratory tests are presented here below.

4.2.1. Packing materials

Three different packing materials were used in this study:

- An organic material obtained by mixing pig manure compost and sawdust named “compos” in this study.
- A natural fibre called “luffa” sponge obtained from the fruit of *Luffa cylindrical* plant and used as a stage in the hybrid system.
- A commercial granular activated carbon (AC).

4.2.1.1. Compost

This packing material was supplied by the Spanish company SLIR S.L. (Specialized Engineering in Recycling Agricultural Residues). Its commercial name is ABONLIR. This material is a compost obtained by mixing pig manure and sawdust and is manufactured in pellets shaped by mechanical compression without the addition of any chemicals. The compost was sieved in order to only keep the pellets whose diameter was greater than 4 mm to fill the systems in order to prevent excessive pressure drop (Swanson *et al.*, 1997). Table 4.6 shows certain chemical and physical properties of this material.

Table 4.6 Physical and chemical properties of the compost using as packing material (Barona *et al.*, 2005; Prenafeta-Boldú *et al.* 2012**)**

Property	Value
Physical parameter:	
Bed apparent density (g m^{-3})	0.98 ± 0.07
Pellet apparent density (g mL^{-1})	1.29 ± 0.08
Material real density (g mL^{-1})	2.72 ± 0.21
BET superficial area (m^2 g^{-1})	12.06 ± 0.09
Langmuir superficial area (m^2 g^{-1})	17.41 ± 0.74
Micropore area (d < 20 Å) (m^2 g^{-1})	0.3
Chemical composition:	
Total organic matter (%)[a]	72
Labile organic matter (%)	40
Total carbon content (%)	32
Total nitrogen content (%)	2
Total hidrogen content (%)	3
Total phosphorous content (%)	0.2
Total sulphur content (%)	3
Elemental sulphur content (%)	< 0.1
Sulphate content	< 0.1
Water content (%)	23.2
pH	6.5 – 7.5

(a) Value provided by the manufacturer.

As material compaction was observed during the first part of the study with the ABONLIR compost as shown in Figure 4.4, for the second part, it was decided to use a mix of compost and pozzolan (lava rock) in a ratio of 80% /20% to enhance the structural stability, and therefore the lifespan of the packing material as suggested by Swanson *et al.*, 1997. Pozzolan was used because of its low price, low density, large bed porosity (0.78) and large specific surface area (see Table 4.7). Besides, some authors suggest that pozzolan could limit drying effects and consequently the development of preferential pathways (Dumont *et al.*, 2008).

Figure 4.4 Photographs of the pelletized compost agglutinated.

Table 4.7 Properties of the Pozzolan (provided by Phenix International)

Parameter	Value
Bulk density (Kg m^{-3})	1500
pH	6.5
Moisture content (%)	21
Water retention capacity (%)	19
Specific surface area (m^2 m^{-3})	578
Particle size (mm)	4-7
Bed porosity	0.78
Silicon dioxide (%)	43.4
Aluminium oxide (%)	14
Iron oxide (%)	12
Calcium oxide (%)	10.8
Magnesium oxide (%)	9.5
Titanium oxide (%)	3
Potassium hydroxide (%)	1.5
Sodium oxide (%)	3.4

4.2.1.2. Luffa sponge

Luffa sponge is a natural material from the Cucurbitaceae plant family that has already been used in the removal of pollutants from wastewater (Ruiz-Marin *et al.*, 2009; Iqbal and Edyvean, 2005). Luffa has a porosity of 0.96 (measured in the laboratory according to the method described by Hodge and Devinny, 1995) and a density of 0.350-0.650 g cm^{-3}. Its fibrous structure was cut into squares of 1.5 cm as shown in Figure 4.5 for packing the column reactor. Scanner electron micrographs (SEM) were taken in order to analyze the structure of the luffa (Figure 4.6). SEM images show a fibrous vascular system with microchannels and small pores where microorganisms can attach.

The aim of using this material was to test it for the first time (to our knowledge) as support material in the biofilters to treat air pollution, considering that it was used before with success in the wastewater treatment.

Figure 4.5 Structure of luffa sponge used as packing material

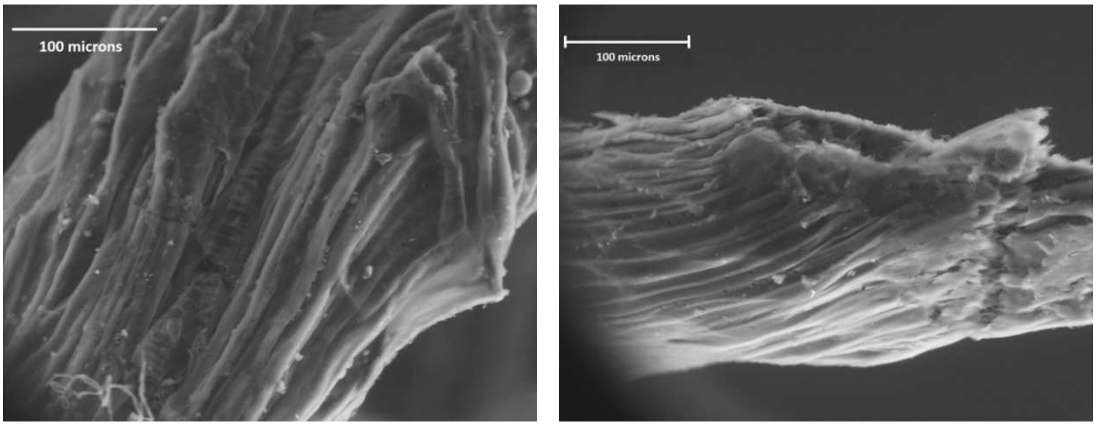


Figure 4.6 Scanning electron micrographs (SEM) of luffa sponge fibres.

4.2.1.3. Activated carbon

The active carbon (AC) used in HS was the C1220 IG 93 Mn from Carbio 12 S.A. This carbon is chemically impregnated for the preferential adsorption of gaseous pollutants like formaldehyde, ketones and alcohols. Normally, activated carbon exhibits no particular affinity for these molecules. This is why AC impregnated with Manganese (Mn) was used in this study. Their properties are presented in Table 4.8.

Table 4.8 Technical data sheet of C1220 IG 93 Mn (from Carbio 12 S.A.)

Characteristic	Value/description
Made from	coconut shell
Impregnation/over chemical activation	yes
Bulk density (ASTM[a] D 2854)	0.50-0.55 kg L^{-1}

Characteristic	Value/description
Ash content (ASTM[a] D 2866)	5-6%
Moisture (ASTM D[a] 2867)	6-8%
pH value (ASTM[a] D 3838)	4-5
BET surface area	1000-1050 m^2 g^{-1}
Iodine value (ASTM[a] D 4607)	1100-1200 mg g^{-1}
Hardness (ASTM[a] D 3802)	97%
CTC adsorption value (ASTM[a] D 3467)	60%
Benzene adsorption value	38%
Specific adsorption (aldehydes/acetic acid)	39%/21%
Using for	Organic acid gas, formal, aldehydes and alcohols

[a] ASTM International standards

4.2.2. Experimental conditions during the acclimation period of the compost material at ppm levels (Spain).

Two litres of an aerobic activated sludge from a wastewater treatment plant (Muskiz-Bizkaia, Spain) were collected and allowed to decant; then 250 mL of the clarified liquid were taken and added to a nutrient solution described previously by Elías *et al.* (2010). This solution was used as inoculum for the compost ABONLIR which was irrigated before it was packed in a Plexiglass column with 10 cm of internal diameter and a total bed height of 30 cm (two sections of 15 cm each one). Setup is represented in Figure 4.7.

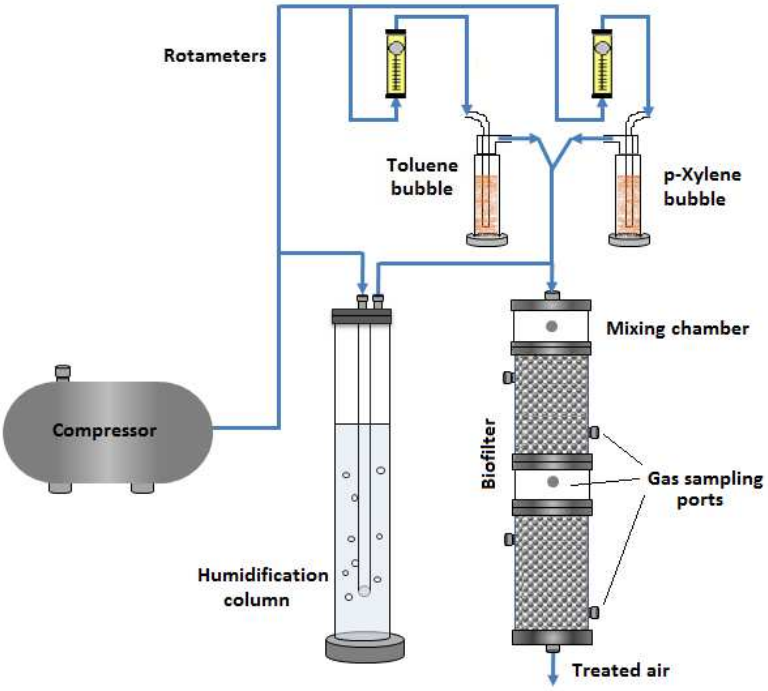


Figure 4.7 Experimental setup for inoculation and acclimation processes.

In this point, the acclimation process is based on the previous exposure of microorganism (already present in packing material and in the sludge) to high gas VOC concentrations. Average inlet loads of 15.2 g $m^{-3}h^{-1}$ for toluene and 4.5 g m^{-3} h^{-1} for p-xylene were introduced into the system. The total air flow rate was maintained in the range of 0.8-1.2 L min^{-1}, corresponding to EBRT from 120 s to 180 s. Operating conditions are summarized in Table 4.9.

Table 4.9 Operating conditions for acclimation period.

Reactor	**Pollutants**	**Concentration**	**EBRT (s)**	**Air velocity ($m\ s^{-1}$)**	**$T_{ambient}$ (^oC)**	**$RH_{inlet\ air}$ (%)**
Acclimation biofilter	Toluene *p*-Xylene	27-108 ppm 4-21 ppm	120-180	0.0017-0.0025	15-25	100

Toluene and p-xylene compounds were continuously analyzed with a micro-gas chromatograph (CP 4900, Varian, The Netherlands) equipped with auto-sampling injection, TCD detector and using He as a carrier gas. The Micro GC was equipped with CP-Sil 5 CB (6m x 0.15mm x 2µm) and CP PoraPLOTQ (10m x 0.25mm x 8µm) columns. The oven, injector and TCD detector were maintained at 90°C, 110°C and 90°C, respectively. The humidity was measured in a thermobalance (HB43-S, Mettler Toledo, International Inc.). CO_2 production was measured with an infrared gas detector (Guardian Plus, Edinburgh Instruments).

4.2.3. Operating conditions of the systems treating ppb concentration levels (representing indoor air pollution)(France)

This part of the materials and methods is based on the setup presented in the Figure 4.8 which is divided in three parts (Polluted gas generation, treatment systems and analytical device). In section 4.2.3.1, the generation of the polluted airstream (at ppb concentration levels) is presented. After its generation, it is diluted in a mixing chamber to finally be divided in two identical streams; one of those goes throughout the BF (biofilter) and the other feed the HS (hybrid system). The subsection 4.2.3.2 presents the analytical equipment used to monitor the performance of the system. Air flows were controlled by the means of mass flowmeters (MS) (Brooks Instrument, 1 % accuracy) installed downstream. Temperature (T) and relative humidity (RH) were measured in real time every fifteen minutes in different point of the systems, using KIMO transmitters connected to the Agilent 34970A Data Acquisition Switch Unit; T and RH data were displayed and analysed by the Agilent BenchLink Data Logger Pro software. The section 4.2.3.3 presents how particles emissions measures were carried out. Description of the treatment systems BF and HS designed in Figure 4.8 is presented here below.

The treatment of a mixture of pollutants was carried out in a laboratory scale plant consisting of two reactors operated in parallel at identical operating conditions (see Table 4.10): a biofilter and a hybrid system (bioreactor + adsorption column) were installed. Both reactors were made of glass sections with a 0.1 m inner diameter and 0.25 m total height. BF was packed with 3.8 L of a mix of compost and pozzolan at a ratio of 80 %/20 % v/v while the filtering media of the hybrid unit consisted of 3 layers (separated between them by a space of about 15cm): the first layer was packed with 1.26 L of a mix of compost and pozzolan; the second layer with 1.26 L of luffa and the third layer with 1.26 of activated carbon. The glass sections have an aperture in the middle to take measures of temperature or samples of the packing material. An additional 10 cm head space was used for the treated air outlet, for irrigation and for measurements of concentrations and relative humidity; an additional 10 cm bottom space was used for the waste air inlet, leachate recuperation and measures of concentrations and relative humidity. The bioreactors were operated in a counter-current configuration.

An additional study was carried out in order to optimize the EBRT which is a crucial parameter determining the filter size for a given air flow (cf. Table 4.3). A contaminated air with an average concentration of 147 ppb (556 µg m^{-3}) of toluene and 86 ppb (375 µg m^{-3}) of p-xylene was treated by a biofilter similar to BF system shown in Figure 4.8. The air flow was changed (20, 30 and 37.5 L min^{-1}) in order to get three different EBRTs: 12 s, 8 s and 6 s. In this case a mix of compost (ABONLIR) with neither inoculation nor acclimation and acclimated compost was used in order to compare the acclimation period at concentrations 10^3 lower than those used in acclimation trials (cf. 4.2.2).

The operating conditions of the different systems are presented in Table 4.9.

Table 4.10. Operating conditions.

Reactor	**Pollutants**	**Concentration**		**Support**	**EBRT(s) (±1.1%)**	**Days**	**T$_{ambient}$ (°C)**	**RH$_{inlet\ air}$ (%)**
		ppb	µg m^{-3}					
BF	Toluene *p*-Xylene	2-45 1-33	7.6-172 4.4-145	Compost[a]	15-23	155	18-34	34-88
HS	Toluene *p*-Xylene	2-45 1-33	7.6-172 4.4-145	Compost[a] Luffa AC	2.5-23	155	18-34	34-88
BF $_{EBRT\ study}$	Toluene *p*-Xylene	147 87	556 375	Compost	12 8 6	60	20 ± 2	40± 4

[a] Compost mixed with pozzolan (80%/20%)

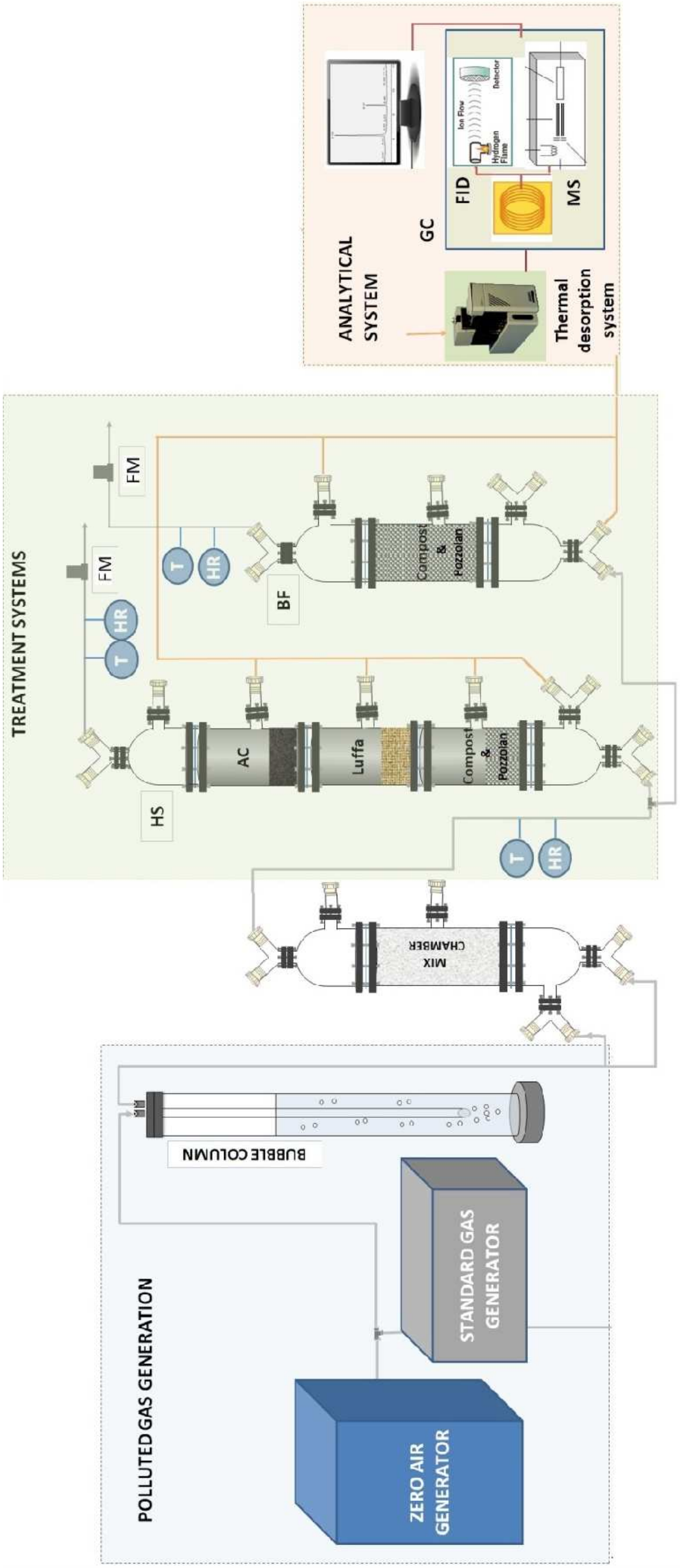


Figure 4.8 Schema of the pilot plan.

4.2.3.1. Polluted gas generation

High-purity air was produced by a zero air generator from NITROCRAFT ® (NCZ 040 R) which produces a constant flow of hydrocarbon free air using a catalyst reaction at high temperature. Compressed air is filtered to guarantee that the air contains no particles, water or oil. Then, a catalytic chamber removes hydrocarbons; after that, the stream is cooled and a final filter removes the residual particles. The NCZ 040 R generates up to 40 NL min^{-1} which is divided between the permeation device (described below) and the dilution current.

The polluted stream was generated via a permeation device. There are several methods for generating VOCs gas standards at very low concentrations which include continuous syringe pump injection, diffusion, evaporation, electrolytic and permeation methods (Koziel *et al.*, 2004). But permeation is the most accurate and reliable method to produce known gas concentrations at the ppb level (Li *et al.*, 2012).

The device used in this study was a PUL 200 (Calibrage, S.A.R.L.) consisting of two thermostatic chambers (adjusted temperatures have an accuracy of +/- 0.1 °C) where sealed polymeric tubes containing the pollutants are placed. The substance is held in liquid/vapor phase equilibrium inside the tube. The permeation process involves a constant gas flow which leads to the pollutant diffusing through the polymer wall and releasing out of the chamber at a constant rate for a given temperature (Figure 4.9).

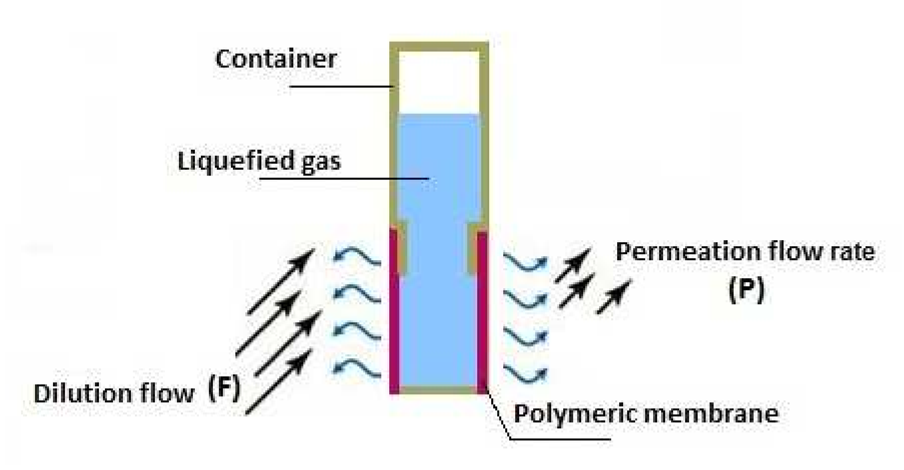


Figure 4.9 Permeation principle

The relationship between permeation rate and concentration is given by the following equation:

$$P = \frac{C \times F}{\frac{22.4}{M}}$$ Equation 4.2

Where,

- P is the permeation rate (ng min^{-1})

- C is concentration (ppm)
- F is flow rate (mL min^{-1})
- M is molecular weight (g mol^{-1})

The flow rate in the permeation device was fixed at 4.078 L min^{-1} which was controlled by a mass flow controller integrated to the device. In order to decrease the concentrations, a dilution flow was implemented to generate a total flow rate of 30 L min^{-1} which fed all the systems at the same pollutant concentrations. US National Institute of Standards and Technology (NIST) traceable certified permeation tubes (Kin-Tek, La Marque, TX, USA) were used for generating the standard gas of toluene and p-xylene. Features of these tubes are showed in Table 4.11.

Table 4.11 Characteristics of permeation tubes provided by Kin-Tek and used in this study

Compound	Permeation rates (ng min^{-1}) (P)	Length (cm)	Calibration temperature °C	Molecular weight
Toluene	8904; 9066; 9001	10-8	80	92.13
p-Xylene	6141; 5917	10-7.8	80	106.17

Fabrication of permeation tubes

Permeation tubes were fabricated with high purity analytical reagents and PTFE was used as material for the tubes. They were calibrated gravimetrically by continuous weight loss monitoring (Sartorius precision balance MC210P, accuracy of 0.01 %). The mass loss was directly correlated with time and then, permeation rate was obtained from the linear equation of the plotted points (Figure 4.10). The in situ fabrication of tubes allows making economic savings up to 80 %.

These tubes allowed working in the concentration ranges of 48.2-354.6 ppb and 26.9-197.6 ppb for toluene and p-xylene respectively. They were calculated following the equation 4.2 and modifying the flow rate from 4 L min^{-1} to 30 L min^{-1}. Permeation rates are given by the slopes of the linear equations in Figure 4.10.

$$P=\frac{C\times F}{\frac{22.4}{M}}\rightarrow C=\frac{22.4xP}{M\times F}$$

$$C_{toluene}=\frac{22.4\times 6017.4}{92.1\times 30000}=48.2ppb$$

$$C_{p-xylene}=\frac{22.4\times 3864.8}{106.1\times 30000}=26.9ppb$$

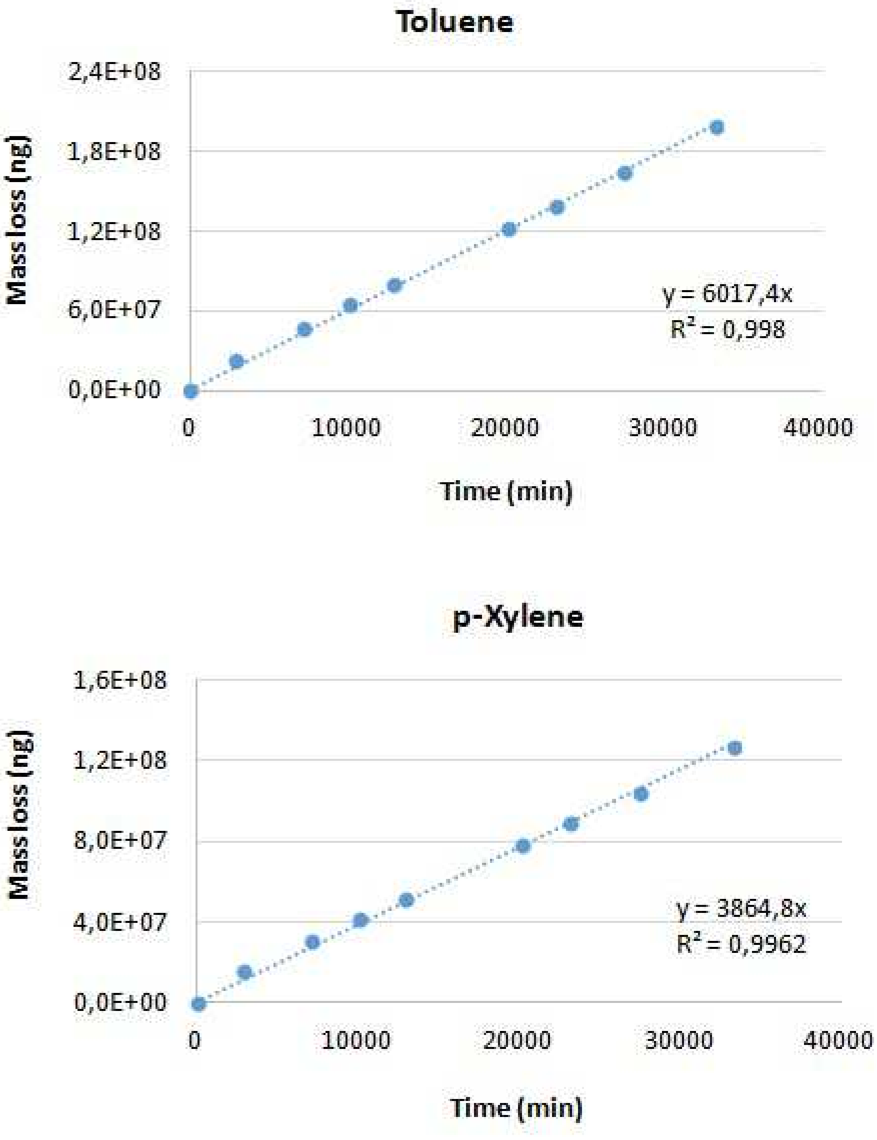


Figure 4.10 Permeation tubes calibration.

4.2.3.2. Analytical system

The analysis of VOCs at levels found in indoor air requires an initial sample pre-concentration to reach those concentration levels. For that reason, a thermal desorption system was used with gas chromatography (GC) coupled to two detectors, a mass spectrometer (MS) and a flame ionization detector (FID).

Thermal desorption system

The UNITY 2 from Markes International is a thermal desorber which operation is cryogen-free thanks to the presence of a 2-stage Peltier cell. As such, a cold trap made from quartz containing a 2 mm diameter x 60 mm long bed of sorbent supported by quartz or glass wool is electrically cooled. The thermal desorber is connected to an Air Server accessory which allows the continuous monitoring of the air streams. The Air Server contains inert switching valves and link tubing to interface the accessory to UNITY 2. It is compatible with gas-phase samples ranging in pressure from sub-atmospheric to 50 psig. Three ports are commonly used for sample, calibrant and zero gas streams, but could just be used for three different samples.

A Nafion® dryer is added to the system to remove water from the stream. It is a copolymer with a sulfonic acid (-SO_3H) terminating the chain which has the ability to absorb up to 13 molecules of water.

Thermal desorption operation

First of all, the system must be purged thoroughly with carrier gas (He) to remove air before heat is applied. Even the smallest trace of oxygen could result in sorbent and possible analyte oxidation, compromising data quality. Then, the gas stream selected is directed out of the Air Server accessory (via the Nafion® dryer) and into the UNITY 2 via the sample tube (Figure 4.11).

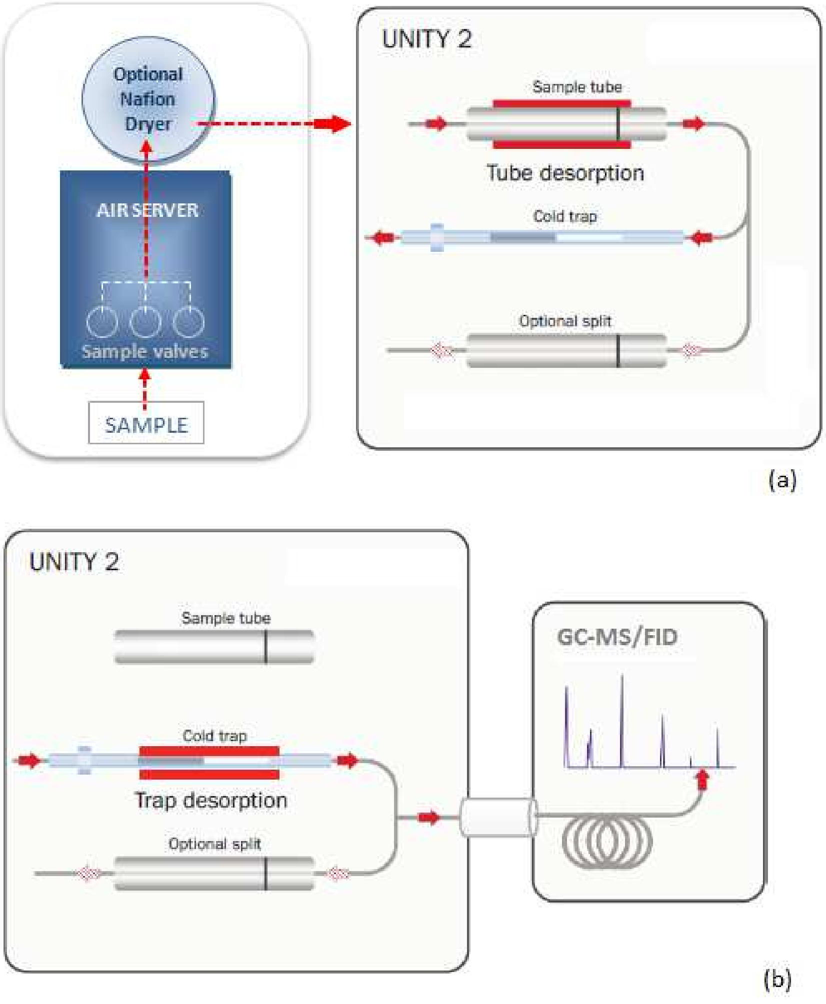


Figure 4.11 Schema of the preconcentration system. Sample tubes desorption (a) and focusing trap desorption (b) during the sample preconcentration.

A primary desorption begins by rapidly heating the sample tube and target compounds are set free to be focussed subsequently in the cryogenic trap (Figure 4.11a). Following primary desorption, carrier gas is flushed through the split tube and the trap to remove any residual air and water prior to trap injection. The final stage is the secondary desorption. The cold trap is heated at a rate of 100°C/s during the first few seconds ensuring rapid desorption of analytes into the carrier gas stream to be then directed to the GC-MS/FID device (Figure 4.11b). Conditions in which this system was operated are presented in Table 4.12.

Table 4.12. Preconcentration settings.

Parameter	Value	Parameter	Value
Pre-sampling		Trapping	
Prepurge time (min)	5	Pre-Trap Fire Purge (min)	2
Split flow (mL min^{-1})	20	Trap Low (°C)	-10
Line purge flow (ml min^{-1})	20	Heating rate (°C s^{-1})	100
Sampling		Trap High (°C)	290
Sample time (min)	5	Trap Hold (min)	3
Post sampling line purge (min)	2	Cmb Flow (mL min^{-1})	20
Post sampling trap purge (min)	2	Minimum Carrier Pressure (psig)	50
Trap flow (mL min^{-1})	20	Flow Path Temp (°C)	200

Chromatograph system

The system consists of a TRACE 1310 Gas Chromatograph (GC) and an ISQ single quadrupole mass spectrometer (MS) (Thermo Fischer Scientific, Inc.). The GC is also coupled to a flame ionization detector (FID).

Gas samples taken at different points of the treatment systems were analyzed by GC/FID and MS. Carrier gas was helium with a flow rate of 1 mL min^{-1}. Chromatographic separations were performed using a Rxi®-624Sil MS column (Restek, USA) 30 m × 0.25 mm i.d., 1.4 µm film thickness. The oven temperature program which has been used to separate VOCs is : (1) hold at 35 °C for 4 minutes, (2) raise at 20 °C min^{-1} to 220 °C, (3) hold at 220 °C for 2 minutes. The temperature of the FID was 300 °C. The transfer line to the mass spectrometer was maintained at the same temperature as the final program temperature of the column. Acquisition in electron impact mode started 4 min after sample introduction (MS detector). The mass range was 30-250 amu (atomic mass unit) and the acquisition rate was half a scan per second. Acquisition was performed in full-scan mode.

Calibration of analytical device

Calibration of the analytical devices (GC/FID) was made using a cylinder gas calibration standard containing a mixture of 100 ppb of toluene and 100 ppb of p-xylene (purity 99.999%) and provided by Messer France S.A.S. The calibration curves are presented in Figure 4.12.

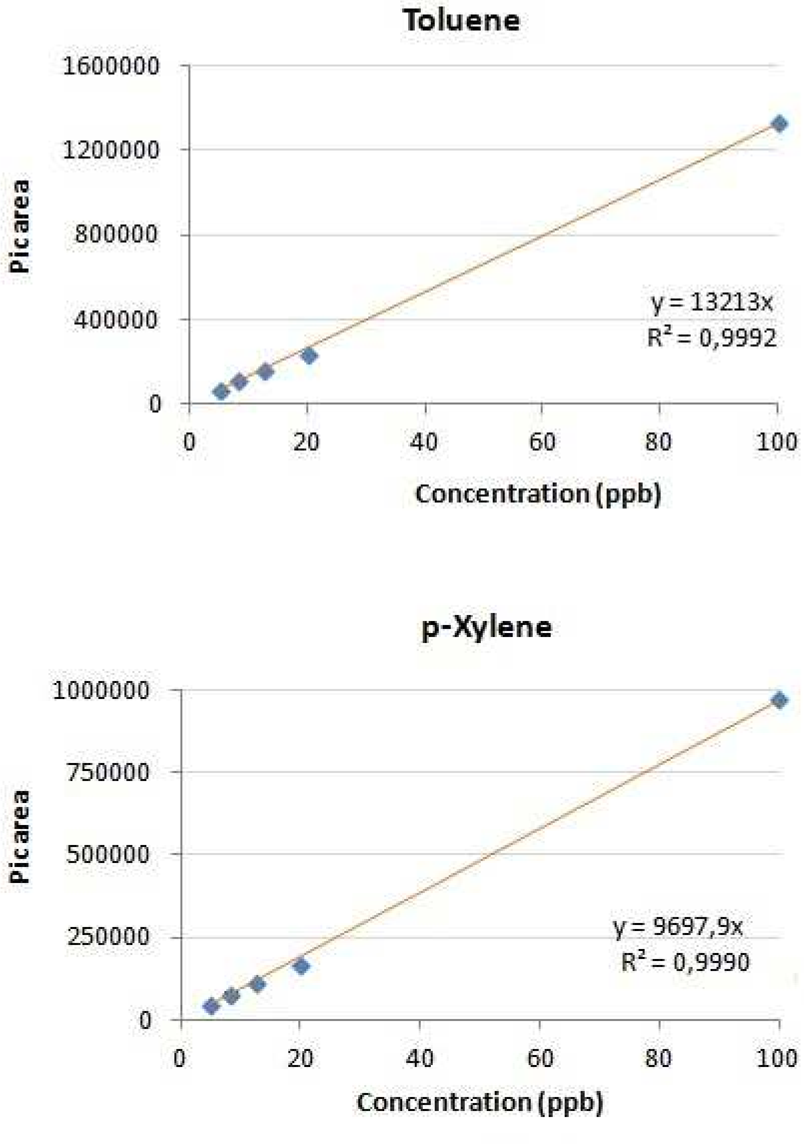


Figure 4.12 Calibration curves for toluene and p-xylene concentration measured in GC/FID

4.2.3.3. Particle emission measurements

Most of the studies that analyse the performance of biofilters are related to the reduction in gas pollutant concentrations reached by those systems. As such, very little is known about the possible emission of particle matter, bioaerosols, microorganism, spores and water which is a controversial subject in indoor environments. Indeed, epidemiological and toxicological studies have identified a connection between Particulate Matter (PM) and adverse health effects (Russell and Brunekreef, 2009; Morawska *et al.*, 2013; Martins *et al.*, 2015). Therefore, an assessment of particle emissions was carried out in this study.

The particle emissions were measured by a real-time particle size spectrometer, the ELPI (Electrical Low Pressure Impactor), which measures airborne particle size distribution in the size range of 0.03−10 μm.

The particles in the sample are first charged electrically by ions produced in a corona discharge. Then, the charged particles are size classified in thirteen groups (0.030, 0.060, 0.108, 0.170, 0.260, 0.400, 0.650, 1.000, 1.600, 2.500, 4.400, 6.800, 9.970 μm) by the low pressure impactor and collected in a specific impactor stage (from the thirteen stages according with size rage) which produces an electrical current. This current is proportional to the number of particles collected, and thus to the particle concentration in a particular size range.

4.2.3.4. Pressure drop

Pressure drop in a biofilter is indicative of an increase in airflow resistance in the bed which is related to bed compaction (Delhoménie and Heitz, 2005). As during the first part of this study material compaction was observed (4.2.1.1), a previous study carried out in the laboratory recorded the pressure drop for the compost and the pozzolan at different air velocities (Gracy *et al.*, 2006) (Figure 4.13). According to the Figure 4.3, using only compost can result in a pressure drop of about 30 Pa but this pressure drop is much less for the pozzolan. Thus, the pozzolan was used as a bulking agent to increase porosity and reduce clogging phenomena across the biofilter bed.

The pressure drop across both reactor columns was found to be about 2mm of water (≈20 Pa) throughout the experimental period. The addition of 20 % of pozzolan to the compost allowed reducing in 33 % the pressure drop with relation to the values presented in Figure 4.3. The absence of changes in bed height can also corroborate the low bed compaction and in turn, the low pressure drop. In fact, this value is low considering that typical pressure drop values in pilot plants have been reported to be between 15 and 460 Pa m^{-1} during a long term operation (Maestre *et al.*, 2007).

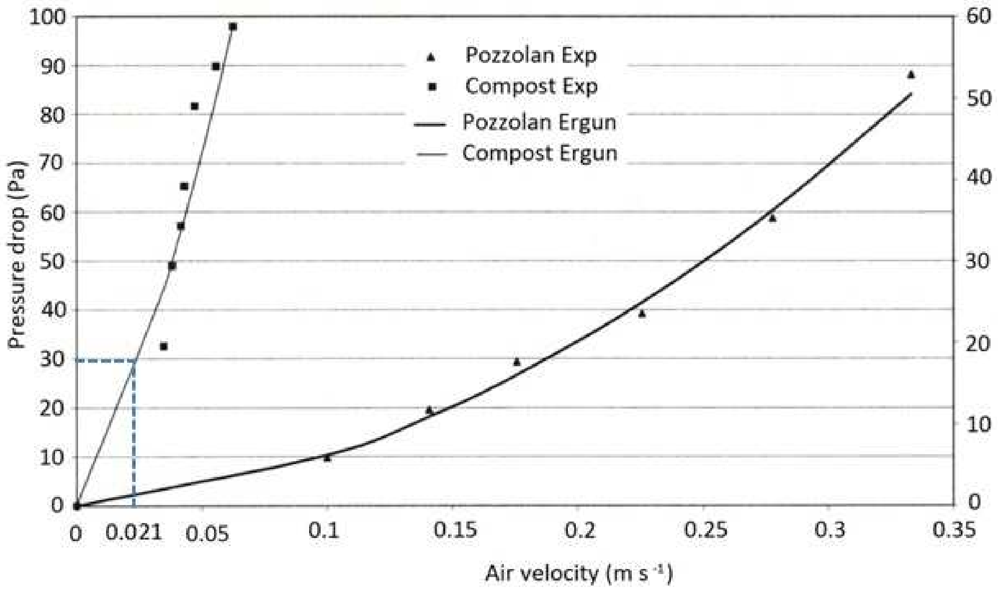


Figure 4.13 Pressure drop for compost and pozzolan at different air velocities (From Gracy *et al.*, 2006).

4.2.3.5. Temperature

Inlet air temperature varied over the time with ΔT = 16 °C. Changes in temperature can affect the bioreactor performance due to the possible inactivation of microorganisms if changes are abrupt (Devinny *et al.*, 1999). On the other hand, increasing temperature can result in the acceleration of biological reactions. Yoon and Park (2002) found that the removal efficiency of a mixture of VOCs (including toluene and xylene) treated in a peat biofilter was higher at 32°C than at 25°C when VOCs concentration was 92 g m^{-3}. Moreover, Rahul *et al.*, 2012. concluded that the removal of BTEX increased when temperatures increased from 15 to 25°C following an exponential trend. In fact, Delhoménie *et al.* (2005) stated an optimum temperature interval (20°C-40°C) considering that in most cases a mesophilic microbial community is developed in biofilters. In the present study, temperatures were between 18 °C and 34°C (see Figure 4.14) which are optimum temperatures for the degradation of the target pollutants, so this parameter should affect positively the bioreactors' performance.

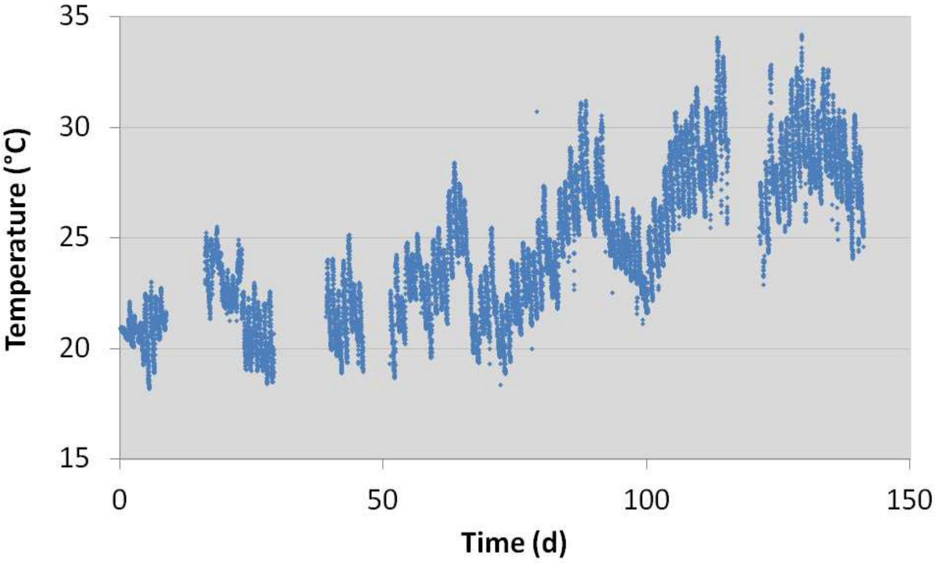


Figure 4.14 Evolution of ambient temperature during the experimental period.

4.2.3.6. Relative humidity (RH)

Inlet air RH varied also over the time. A minimum value of 2.6% and a maximum of 87.9% were registered (Figure 4.15). Average relative humidity was 51.0%. Packing material water content is highly affected by this parameter because the drying of the material could be accelerated by low inlet air humidity. Controlling this parameter during laboratory tests was difficult due to ambient temperature changes, condensation phenomena and heat loss in the humidification column.

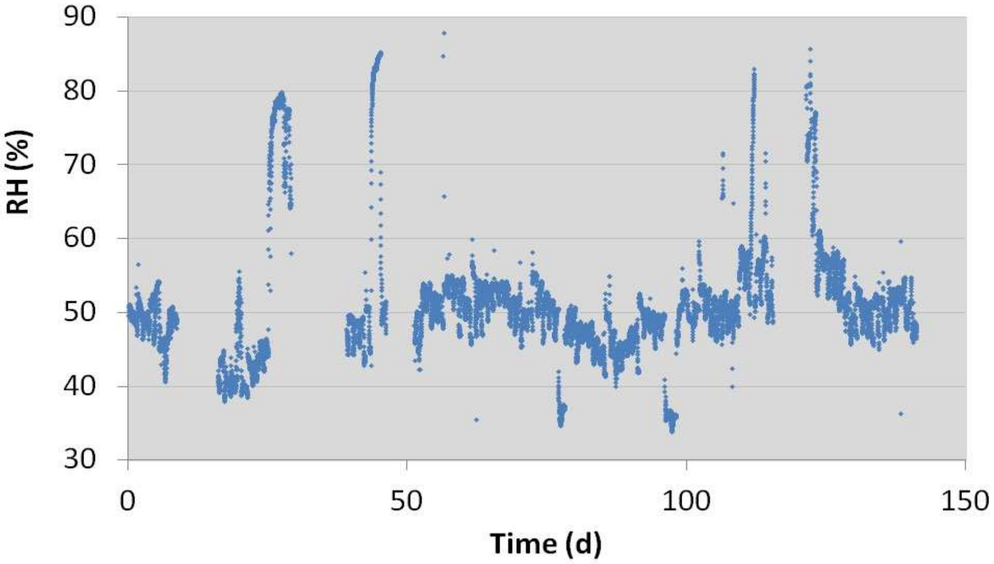


Figure 4.15 Evolution of relative humidity in the inlet stream.

4.3. Results and discussion

Results will be divided in three subsections concerning: (i) packing material study; (ii) acclimation trials at ppm concentration levels and (iii) experimental trials at ppb levels.

4.3.1. Packing material (compost)

4.3.1.1. Evolution of the compost moisture content

The moisture content of biofilter media is a key parameter influencing its performance. A better understanding of the support drying is necessary in order to properly control the wetting process because the excess of water reduces biofilter porosity, which in turn favours the formation of anaerobic zones, increases pressure drop, and prompts the leaching of biomass and nutrients (Morales *et al.*, 2003). On the other hand, low moisture content promotes the formation of preferential flow channels in the biofilter bed and reduces the metabolic activity and transfer of pollutants from gas phase into the biofilm (Auria *et al.*, 1999)

To study drying phenomenon, packing material was immersed in water for 48 hours (time considered enough to saturate material based on previous trials). Then it was dried with an air at 0 % of relative humidity and a velocity of 0.021 m s^{-1}. The temperature was maintained at 17.6 °C ± 2.5 °C. According to Figure 4.16, 9 days (216 h) were necessary to obtain a stabilized outlet relative humidity (RH) which means that all no-tightly bound water was removed from the support. Figure 4.16 also presents the quantity of evaporated water which was calculated following the algorithm presented in the Appendix A.

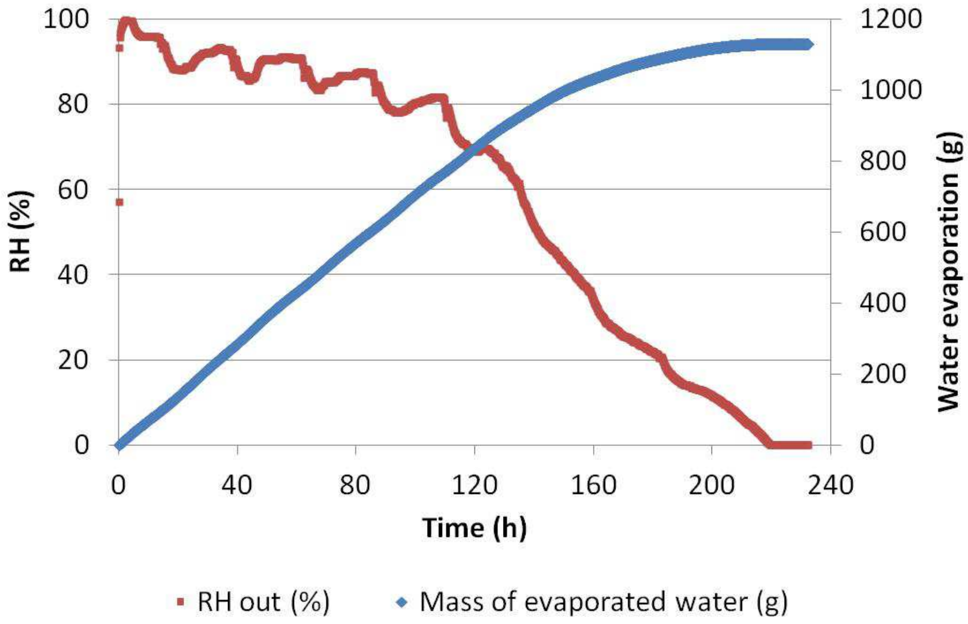


Figure 4.16 Relative humidity decrease during packing material drying.

Based on evaporated water data, the evolution of the material moisture content was calculated (Figure 4.17). Initially, the packing material had a moisture content of 26.5 % ± 0.2 % which is considered a low value according to some authors (Shareefdeen *et al.*, 2010; Gaudin *et al.*, 2008; Auria *et al.*, 1998; Cox *et al.*, 1993). Figure 4.17 shows that dry-basis moisture content (X) decreases linearly with time the first 130 hours followed by a non-linear decrease period (70 hours) until the material reaches its equilibrium moisture content (X_{eq}). At the end of the experiment, only 1 % of the initial moisture content remains inside the material. In this case, the drying process depends mainly on the internal transport limitations of the material being dried and not on external heat and mass transfer (Mujumdar, 2011).The derivative of the equation of this curve gives the water evaporation rate expressed in g of water evaporated per g of dried material per hour.

In order to establish a good frequency of irrigation and considering that compost has low moisture content, its drying should be avoided. The minimum desired value for material water content (dry basis) was fixed at 0.20 $g_{water}\ g^{-1}_{dried\ material}$. Hence the irrigation should be performed every 48 hours according to the Figure 4.17. This assumption was validated during the laboratory tests related to the treatment of toluene and p-xylene at ppb concentration levels. The evolution of the material moisture content was calculated during 72 hours. Results are presented in Figure 4.18. In real conditions, moisture content was in effect kept over 0.20 $g_{water}\ g^{-1}_{dried\ material}$ even at 72 hours without irrigation. The quantity of water to be added to the biofilter per irrigation is given by the green curve in Figure 4.18. In brief, 165 mL of water were added per irrigation every 3 days to the BF system and 55 mL to the compost stage of the HS.

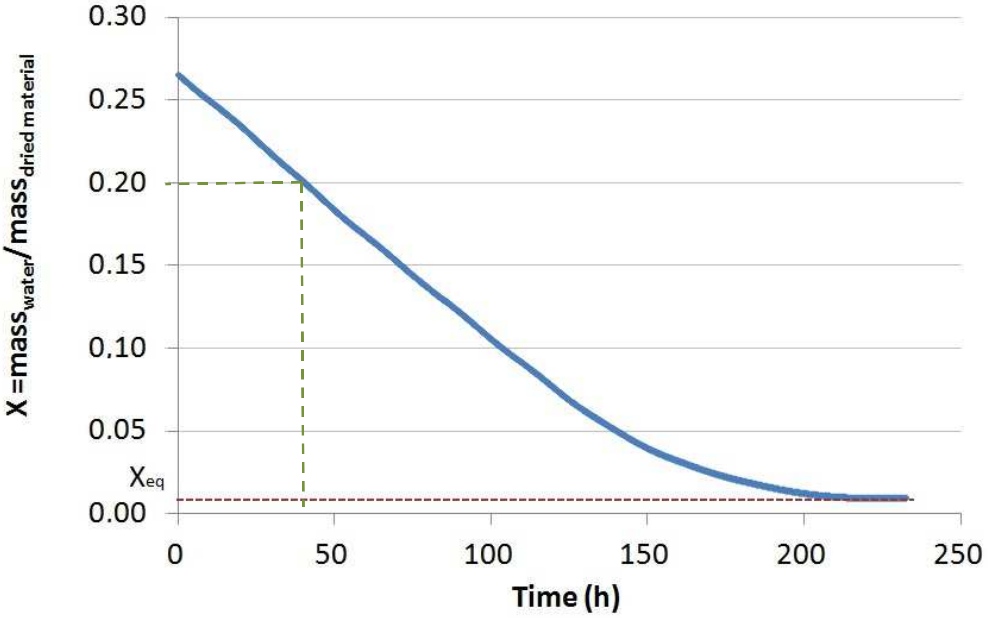


Figure 4.17 Evolution of the material water content (dry basis).

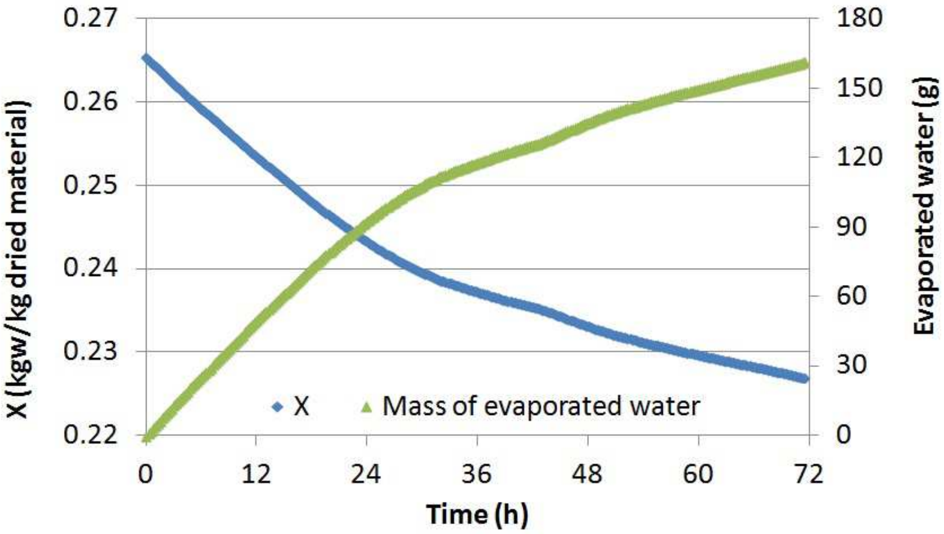


Figure 4.18 Evolution of the compost-puzzolan water content (dry basis) and the quantity of evaporated water.

On the other hand, the equilibrium between the mixture content of the wet material and the relative humidity can be represented by sorption isotherms (Pujol *et al.*, 2010). Figure 4.19a shows the general shape of the typical sorption isotherms. Generally, three zones, A, B and C, can be distinguished. They point out the different water binding modes on the solid material. In region A, there is a lower water activity, due to the tightly bound water, unavailable for reaction, and monolayer adsorption of water. In region B, the water is more loosely bound and is confined in smaller capillaries. Region C corresponds to free water in pores and which is available for reactions and as a solvent (Mujumdar, 2011).

In the case of the experimental isotherm and considering it is a desorption process, two zones can be distinguished (Figure 4.19b). The first zone (C) represents the free water which will be available for microorganism and therefore, moisture content should be maintain in this range during the biofiltration test. The second zone (A+B) corresponds to the bound water; the surface moisture content decreases and consequently, the mass transfer coefficient decreases as well. Accordingly, the moisture content in the compost material should not decrease below 6 % because the loss of activity might be irreversible and the re-wet difficult. Consequently, humidification of the inlet air stream was performed as well as periodic irrigation as described above.

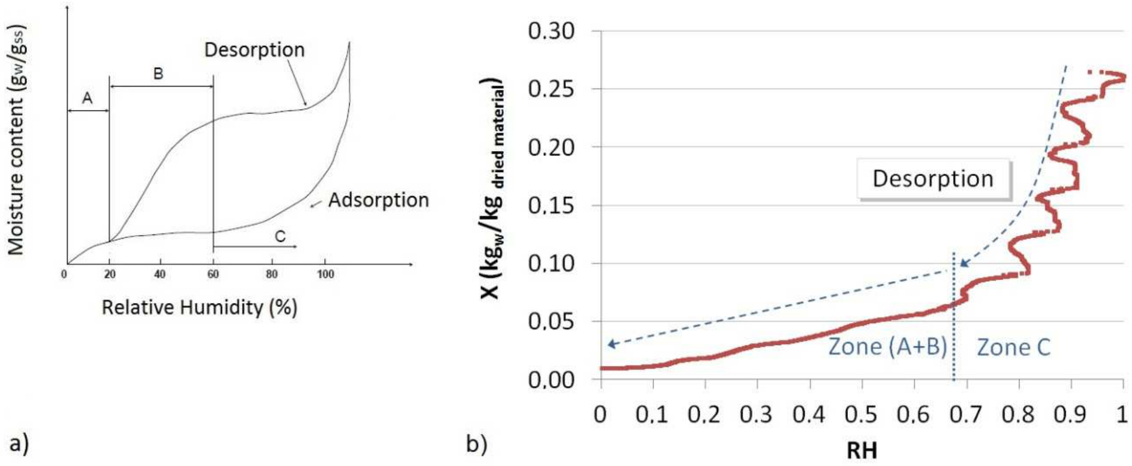


Figure 4.19 Sorption isotherms: a) typical sorption isotherm (Mujumdar, 2011); b) compost desorption isotherm.

4.3.1.2. Evolution of the biological and chemical parameters of the compost

Laboratory analyses of the compost material were perform by the Laboratoires des Pyrénées et des Landes (France) before the operation at ppb concentration levels (compost exposed at ppm concentration levels) and after an operation time of 80 days. Results are shown in Table 4.13.

Table 4.13. Evolution of the biological and physico-chemical parameters of the organic packing material (ABONLIR) exposed to low contaminant concentration levels (ppb).

Parameter	**t = 0**	**t = 80**
Fungal flora (CFU g^{-1})	1600	810
Aerobic microorganisms (CFU g^{-1})	48x10^{6}	24x10^{5}
Sulphate-reducing bacteria (CFU g^{-1})	40	<10
Sulphates (mg kg$^{-1}_{\text{dry material}}$) (±1 mg kg^{-1})	10442	4009
Ammonium (g kg^{-1} $_{\text{dry material}}$)	0.42	0.08
Phosphorous (mg kg^{-1} $_{\text{dry material}}$) (±1 mg kg^{-1})	421	8660
Total organic carbon (g kg^{-1} $_{\text{dry material}}$) (±3%)	124.2	118.9
Total Kjeldhal nitrogen (g kg^{-1} $_{\text{dry material}}$) (±0.25%)	8.02	5.74
Dry matter content (%)	72.8	80.6
Total volatile matter (%)	21.3	17.4
pH (aqueous extract) (±0.2)	9.01	9.11

Concerning biological parameters, values of aerobic microorganisms are far below the typical bacterial numbers reported in the literature for industrial biofilters (10^{8}-10^{10} per gram of sample) (Devinny *et al.*, 1999). Fungal flora and aerobic microorganism concentration decreased 50 % and 95 % respectively over the time. The reduction in microorganisms in biofilters working at very low contaminant concentration levels was previously reported by Ondarts *et al.* (2010). This behaviour could be explain by the fact that very low pollutant concentrations neither favour the development of new biomass nor help in the upholding of the initial number of colony forming units (CFU). This fact was theoretically explained by Guieysse *et al.* (2008) who demonstrated why at VOCs indoor concentrations the microbial growth is limited.

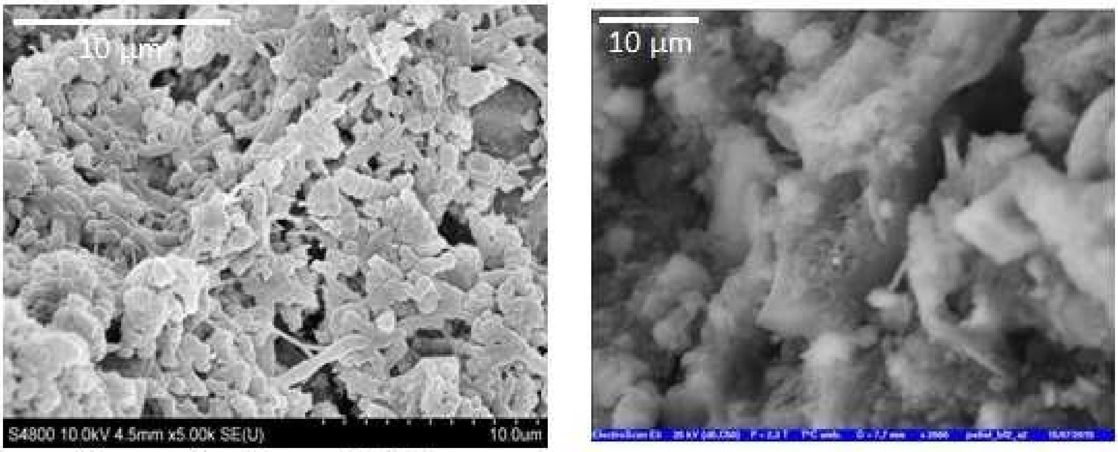
Considering the variation of physicochemical parameters, there is a low diminution in the organic carbon which suggests that the media was not used as carbon source by microorganism. On the contrary, nitrogen diminution could be associated with this phenomenon. A questionable increase was also detected in the concentration of phosphorous.

SEM photographs

SEM images of different packing materials at the initial time (day 0) and at day 80 were taken with an environmental scanning electron microscope Electroscan ESEM E3 at 25 kV (accelerating voltage) and magnification of x250 (Figure 4.20). These photographs show significant differences in the nature and density of the microbial population developed. For the compost, abundant microbial community was present after the acclimation period at ppm concentration levels (Figure 4.20a) but, after 80 days of feeding the biofilter with ppb levels of toluene and p-xylene, a considerable reduction in microorganisms is clear (Figure 4.20b). These findings are in accordance with laboratory results concerning bacteriological analyses which are presented here above (Table 4.13).

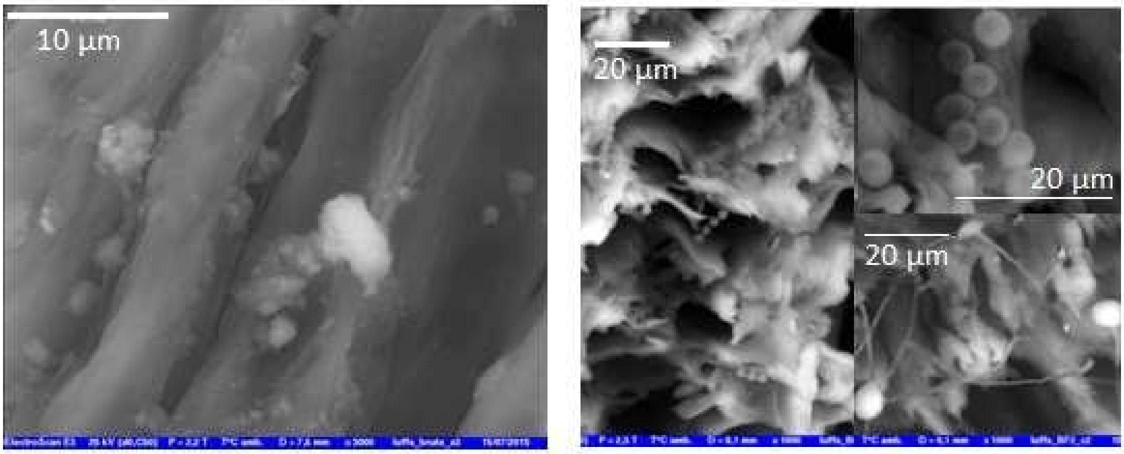
The luffa (second stage of the HS) was not acclimated, therefore no signs of microorganisms activity was seen at the beginning of the experiments (Figure 4.20c). Nevertheless, diverse microbial morphologies including bacteria, mycelia and spores could be identified in SEM photos after 80 days (Figure 4.20d). These microorganisms have certainly been carried away by the flow stream from the compost stage (even if stages were spaced out at 15 cm). The results indicate that the luffa stage did not play an important role in the elimination of pollutants despite the presence of microorganisms. Studies carried out in parallel (results not presented in this report) showed a potential of this material in biotrickling filters where moisture content media is not an issue.

Similar findings can be seen over the AC SEM photos (Figure 4.20e and Figure 4.20f) where no microorganisms were present at the starting period whilst some spores were detected at the end. The potential colonization of the activated carbon by microorganism could be considered as a good opportunity as microorganisms could play an important role in the regeneration of the AC bed.



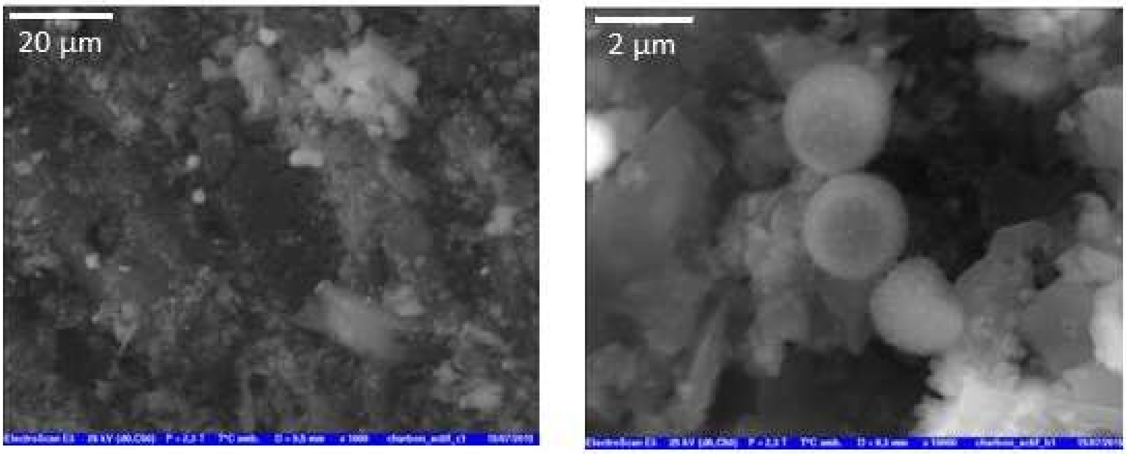
a) After acclimation period at ppm concentration levels

b) After 80 days of BF operation



c) t = 0

d) t = 80



e) t = 0

f) t = 80

Figure 4.20 SEM photographs of packing medias: Compost (a, b); luffa (c, d) and AC (e, f).

4.3.2. Acclimation trials

Keeping stable the pollutant concentrations of toluene and p-xylene during the acclimation period was not possible due to changes in the laboratory ambient temperature (ΔT = 11 °C). Concentration ranges for toluene and p-xylene were 65-275 ppm (245-1040 mg m^{-3}) and 19-89 ppm (83-387 mg m^{-3}), respectively. Despite the variations in inlet concentrations, an increasing trend of the removal efficiency (RE) of toluene was observed over the time as indicated by dashed line in Figure 4.21a.

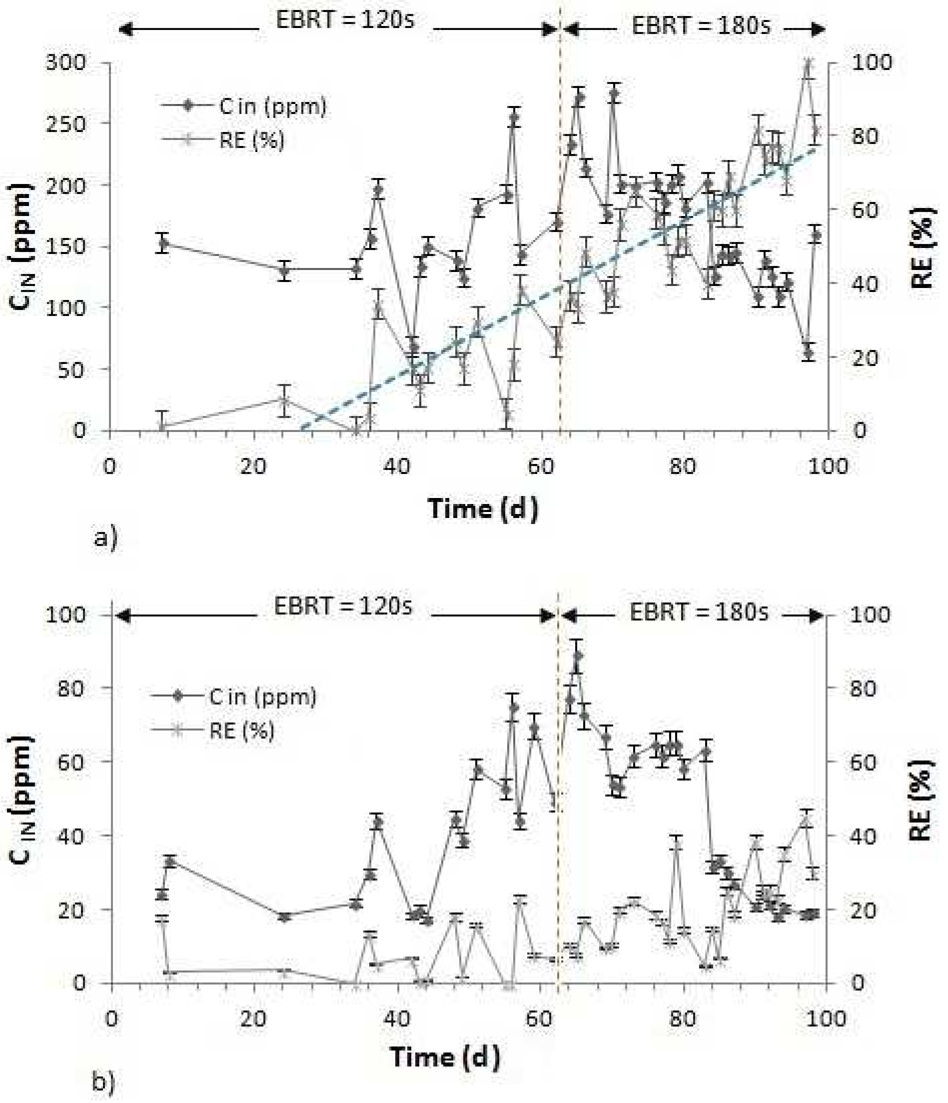


Figure 4.21 Evolution of removal efficiency during the acclimation period of the compost at ppm concentration levels for (a) toluene and (b) p-xylene.

When the Empty Bed Residence Time (EBRT) was increased from 120 s to 180 s due to low removal efficiencies, the toluene removal efficiency reached values >80 %. On the contrary, only a maximum RE of 45 % was achieved for p-xylene (Figure 4.21b) and the average value was just 17 %. Low RE values for p-xylene were also reported by other authors under similar conditions (Gallastegui *et al.*, 2011a; Rondeau *et al.*, 2012; Rene *et al.*, 2012) explained by inhibitory effects among the different compounds present in the polluted airstream. For instance, Gallestegui *et al.* (2011a) found that the p-xylene removal efficiency decreased from 39 % to 18 % due to the increase of toluene in the airstream from 0 to 35.9 g m^{-3} h^{-1}, but the toluene degradation was stimulated when the p-xylene was present. Conversely, Jorio *et al.* (1999) noticed that the toluene biodegradation was inhibited by the presence of xylene while the presence of toluene had negligible effect on the xylene removal efficiency when the inlet concentrations of the contaminants were 2.14 g m^{-3} (567 ppm) for toluene and 1.88 g m^{-3} (432 ppm) for xylene and the EBRT was 102 s.

On the other hand, both acclimation time and EBRT values could be considered quite high compared to those reported by other studies. For example, Mathur *et al.* (2007) reported an acclimation period of 30 days for a system working at average BTEX inlet concentration of 0.4194 g m^{-3} and an EBRT of 2.3 min. Rene *et al.* (2015) treated a mixture of benzene and toluene in a compost biofilter which resulted in a steady removal efficiency of 74 % being achieved on the 18th day for toluene inlet concentration ranged 0.14- 1.48 g m^{-3} (37-392 ppm) and an EBRT of 147 s. The removal efficiency of benzene was maintained at around 68 % during the whole acclimation period. Further data are shown in Table 4.14.

Table 4.14. EBRT and acclimation time in biofilters treating BTEX.

Compounds	Concentrations (g m^{-3})	EBRT (s)	Acclimation time (d)	Reference
BTEX	0.4194	138	30	Mathur *et al.* (2007)
Benzene and toluene	0.14-1.48	147	18	Rene *et al.* (2015)
BTX	3.4	60	<30	Ortiz *et al.* (2003)
Ethylbenzene and toluene	0.5	250	8–10	Gallastegui *et al.* (2013)
BTEX	0.3875	183	18	Rahul *et al.*, 2013
Toluene and p-xylene	0.253-1.104 0.083-0.388	180	100	This study

Despite the compost acclimation was considered incomplete with regard to the p-xylene, this acclimation period was considered as enough to use this “acclimated compost” in the trials at ppb concentration levels.

4.3.3. Results of experimental trials at ppb levels

Firstly, results on the study on the EBRT are presented. Secondly, the results concerning removal efficiencies of a mixture of pollutants at ppb concentrations, in the BF (biofilter) and the HS (hybrid system) are presented. Finally, the generation of by-products, emission of particulate matter and other process parameters are described.

4.3.3.1. EBRT study

Contaminated air with an average concentration of 147 ppb (555 µg m^{-3}) of toluene and 86 ppb (374 µg m^{-3}) of p-xylene was treated by a biofilter as described before in section 4.2.3. The air flow was changed in order to get three different EBRTs: 12 s, 8 s and 6 s. In this case a mix of compost (ABONLIR) with neither inoculation nor acclimation and acclimated pellets (80/20) was used in order to compare the acclimation period at concentrations 10^3 lower than those used in acclimation trials in the previous section (cf. 4.3.2). Results are presented in Figure 4.22.

The acclimation period for the toluene removal exhibits an exponential trend until RE reaches 100% at day 35 (Figure 4.22a). This period is almost three times shorter than that reported for ppm concentrations in the previous trial (100 days). It can be suggest that indigenous microbial population and specific developed bacteria of the compost used in acclimation trial, in conjunction with the nutrient content of the compost, influenced this short lag period. After acclimation, the toluene RE reached 100% for an EBRT of 12 s. A small decrease in RE was registered after EBRT changed to 8 s but 100% RE was recovered and kept it regardless the third change in EBRT. Conversely, the p-xylene removal never exceeded 65% during the entire test, but gradual increases in removal efficiency over the time can be observed on Figure 4.22b which leads to think that the acclimation period had not finished for this pollutant at the end of the experimental trial. Nevertheless, higher p-xylene REs were recorded (65% maximum) than those registered in the case of ppm concentrations (45% maximum) and despite the diminution in RE with every EBRT change, RE increased continuously over the time .

There is little information about VOC biological treatment at trace level concentrations and low EBRTs. Lebrero *et al.* (2011) studied the performance of a biofilter packed with a mixture of compost and perlite in the removal of odorous emissions containing low concentrations of toluene (106-159 ppb) and other compounds. In this case, the toluene was removed over 99.9% regardless of the EBRT tested (94-32 s). This value is comparable to that observed in the present study but the lowest EBRT value tested by Lebrero *et al.* is three to six times higher. Likewise, high toluene removal efficiency (99.3%) was reported by Liu *et al.* (2009) for a compost biofilter treating several VOCs at an EBRT of 40.5 s. At this time, the toluene concentration was 19.5 ppb which is a similar value to that of the present study but EBRT is still high. Considering p-xylene, surprisingly, Liu *et al.* (2009) registered removal efficiencies higher than 94% for concentrations 367-1420 ppb.

Removal efficiencies close to 100% were reported by Ondarts *et al.* (2010) working in a packed biofilter at 20s (EBRT) and treating seven VOCs (including toluene) at concentrations ranged from 32 µg m^{-3} to 140 µg m^{-3}. These data are closer to conditions used in the present study and the EBRT used was the lowest found in literature for biological treatment of very low concentrations of VOCs.

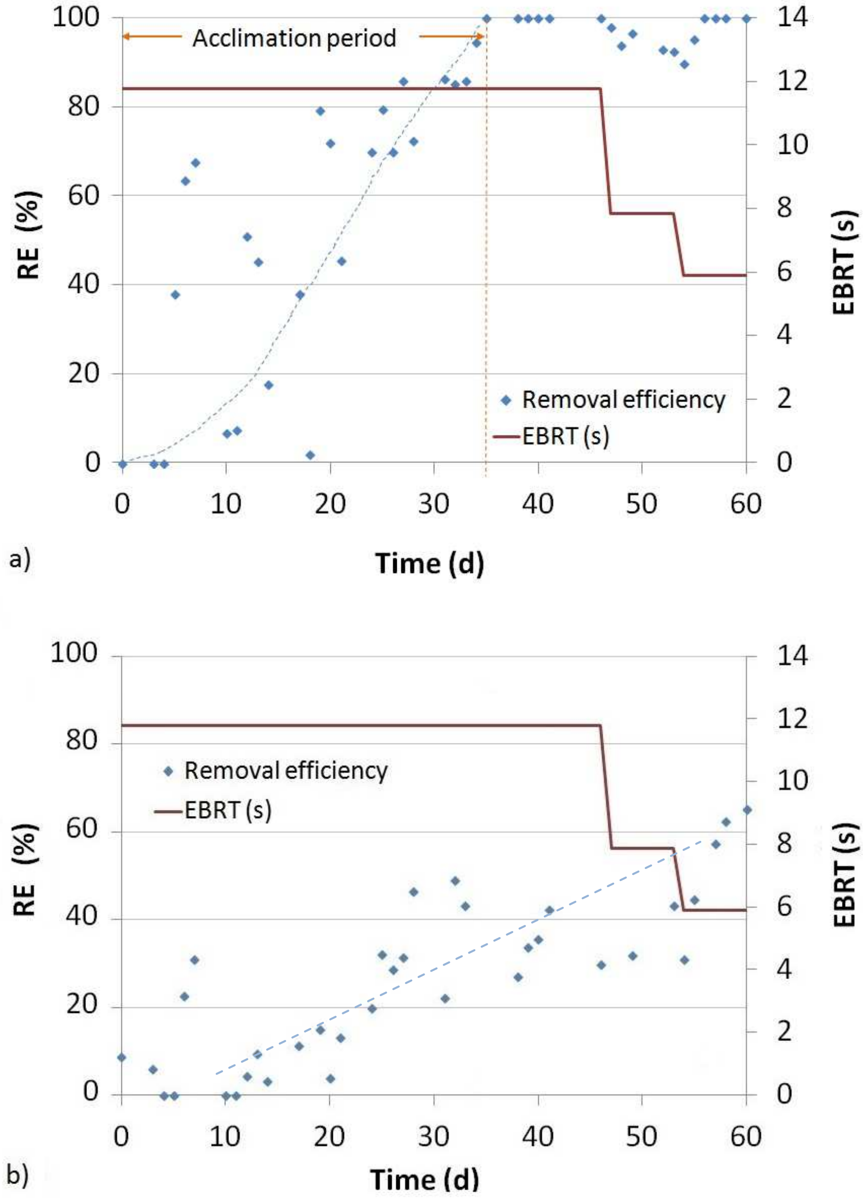


Figure 4.22 Removal efficiency at different EBRTs for (a) toluene and (b) p-xylene.

4.3.3.2. Comparison of systems' efficiency: BF vs. HS.

As described in section 4.2.3 a biofilter (BF) and a hybrid system (HS) (bioreactor+adsorption technology) were implemented in the laboratory in order to treat a contaminated gas stream containing toluene and p-xylene at concentration ranges of 2-45 ppb (7.6-172 $\mu g\ m^{-3}$) and 1-33 ppb (4.4-145 $\mu g\ m^{-3}$), respectively. Results concerning both systems are presented in three subsections:

- Comparison of the BF with the compost stage of the HS
- Overall efficiency of the systems
- Stage removal efficiency in HS

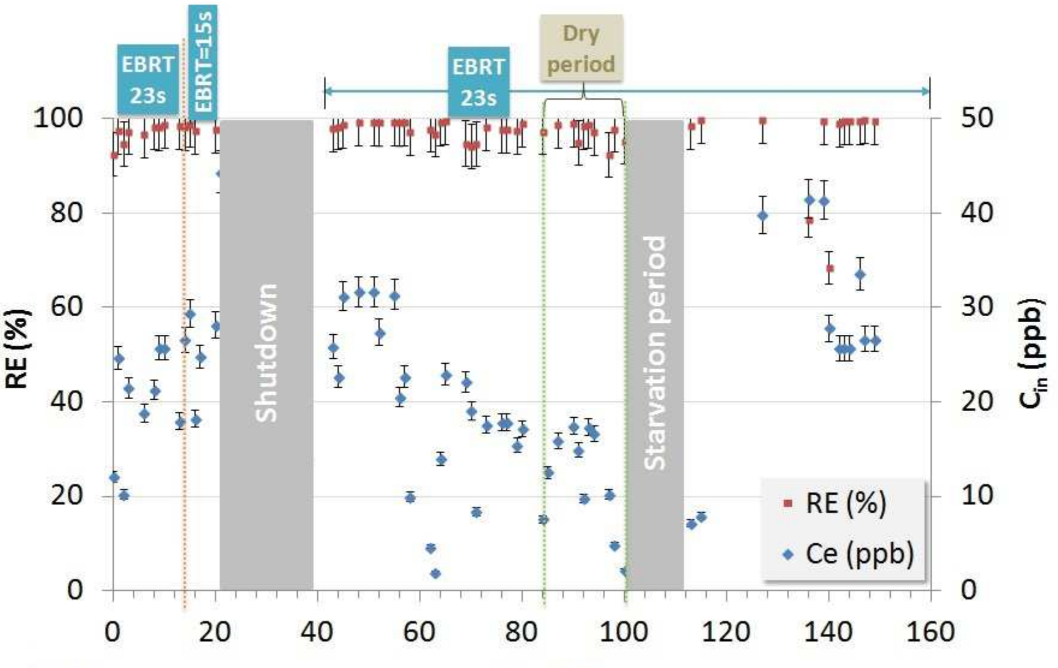
Efficiency of the reactors taking into account only pelletized compost

Both reactors were operated during 150 days and under changes in operational conditions. For the HS system only the stage of compost is taken into account in this section. Pellets of compost used in both reactors were those acclimatized at ppm concentrations. The ability of both systems to recover from changes in EBRT, inlet concentrations, irrigation periodicity (changed from three times a week to once a week) and several days of shutdown (neither air supply nor irrigation) was studied by recording removal efficiencies.

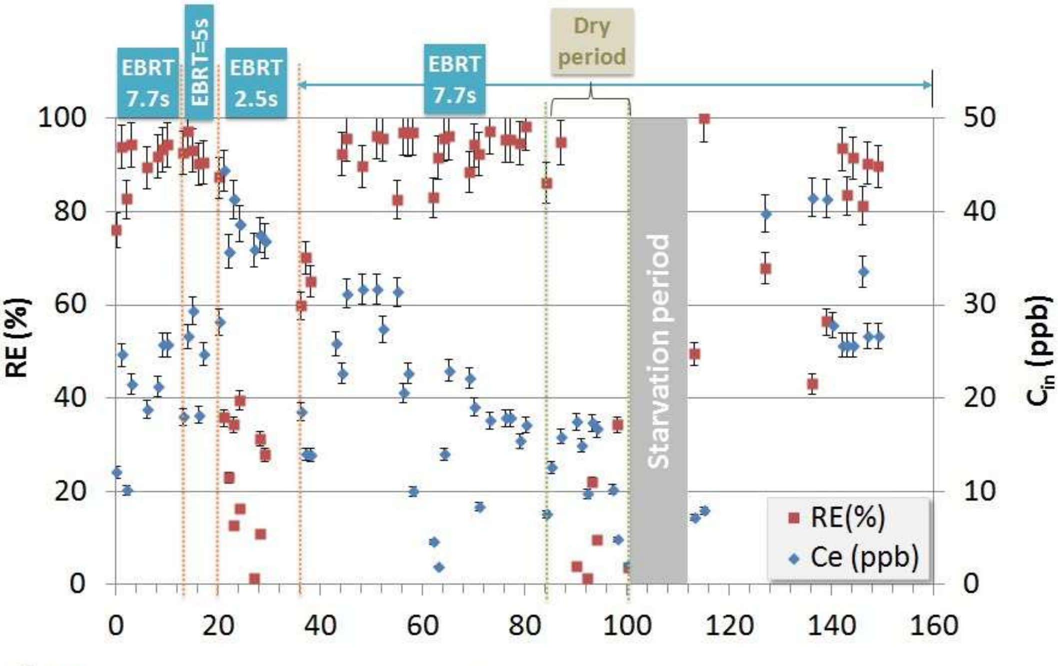
First of all, a rapid acclimation was observed in both systems treating toluene (Figure 4.23a, b) and in BF treating p-xylene (Figure 4.24a) despite the low EBRTs and concentrations compared to those of EBRT study (cf. 4.3.3.1). It could be said that the acclimation strategy herein applied was successful and that a development of an efficient microbial community in the degradation of toluene and p-xylene was reached during the acclimation trials. In the case of p-xylene removal by HS, the lower removal efficiency values observed might be mainly related to the low EBRT in the compost stage which was three times lower than that used in BF (7.7 s and 23 s, respectively).

As can be seen in Figure 4.23a, the toluene removal efficiency in BF remained stable regardless of the changes in operational conditions keeping an average removal efficiency of 97 % over all the operational time. Neither shutdown (from 21th to 39th days) nor starvation period (only humidified air was supplied from 100th to 112th days) influenced its performance. Nevertheless, significant changes in inlet concentration (8 ppb to 42 ppb) from 127th to 139th days affected the removal efficiency which dropped down to 68 %, but higher values were recovered immediately upon the stabilisation of inlet concentrations at around 27 ppb. Removal efficiency during pollutant concentration peaks in biofilters has been reported in literature for biofilters operated at similar VOCs concentrations. For example, Hort *et al.* (2014) observed a decrease in the RE of a biofilter treating toluene during pollutant concentration peaks which was explained by a progressive reduction of the microbial population density. Likewise Lebrero *et al.* (2010) suggest that low performance during pollutant overloading in biofilters was caused by microbial activity rather than by pollutant mass transport limitations.

Regarding the performance of HS (compost stage), it was significantly influenced by operational changes (Figure 4.24b) which is consistent with the very low EBRTs imposed on this system. Nevertheless, even at an EBRT of 5 s ,RE up to 97 % was registered and despite these low EBRTs tested in the system, the average removal efficiency was 70 % at the end of the study. The lack of irrigation is noticeably the most influencing parameter in toluene removal efficiency as values as low as 1 % were registered during this period (day 92). Similar behaviour but, in a less extent, was recorded by Lebrero *et al.* (2010) when irrigation process was interrupted during five days in a biofilter treating VOCs and H_2S. In this case, the toluene RE decreased only by 10 %. Then, after the starvation period (days 100th to 112th) high RE was recovered four days after, but it was again affected by changes in inlet concentration to finally reach a stable value close to 90 % at concentrations of 27 ppb. It should be noted that both systems presented similar recovery capacities for toluene removal after disruptions in operation despite the differences in the EBRT.



a) BF



b) HS

Figure 4.23 Toluene removal efficiency for (a) BF system and (b) stage of compost in HS system.

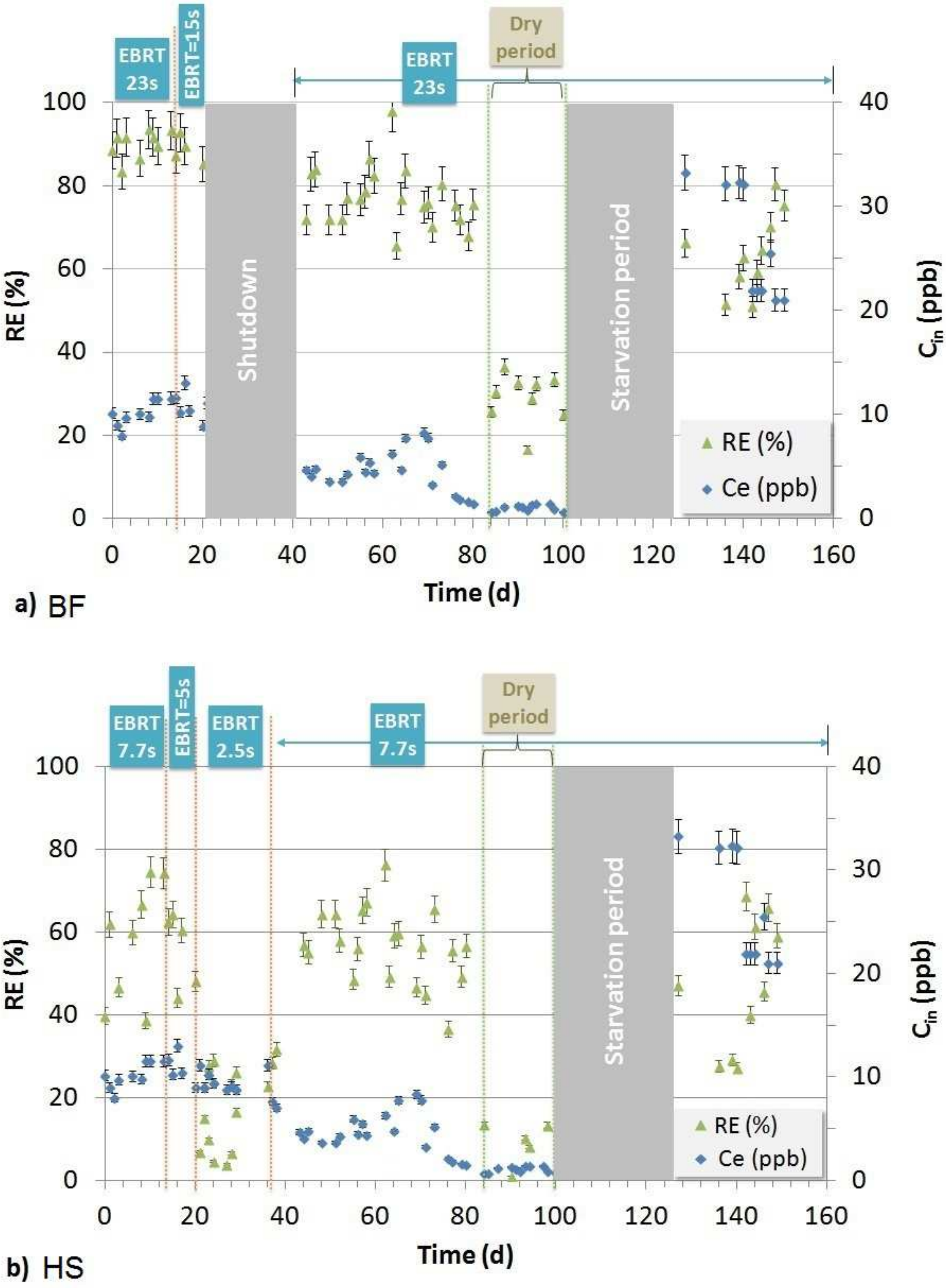


Figure 4.24 p-Xylene removal efficiency for (a) BF system and (b) stage of compost in HS system.

Correspondingly, the p-xylene removal was recorded during the whole experimental time. Values up to 98 % and 76 % were registered in BF and HS, respectively (Figure 4.24a, b). Compared to the p-xylene removal performances presented in the previous experiments, these values were higher. As in the case of toluene, results demonstrated that the BF was able to better withstand operational changes in comparison to the HS, although both systems were affected in a similar way during dry period. Removal efficiencies dropped suddenly in the same proportion which was not the case for toluene removal in BF where RE remained constant in drying conditions (Figure 4.23a). Poor p-xylene elimination capacity during dry periods was also recorded by Gallastegui *et al.* (2011b). After starvation period and, although the inlet concentrations were increased, a rapid recovery in removal efficiency can be noticed in both systems.

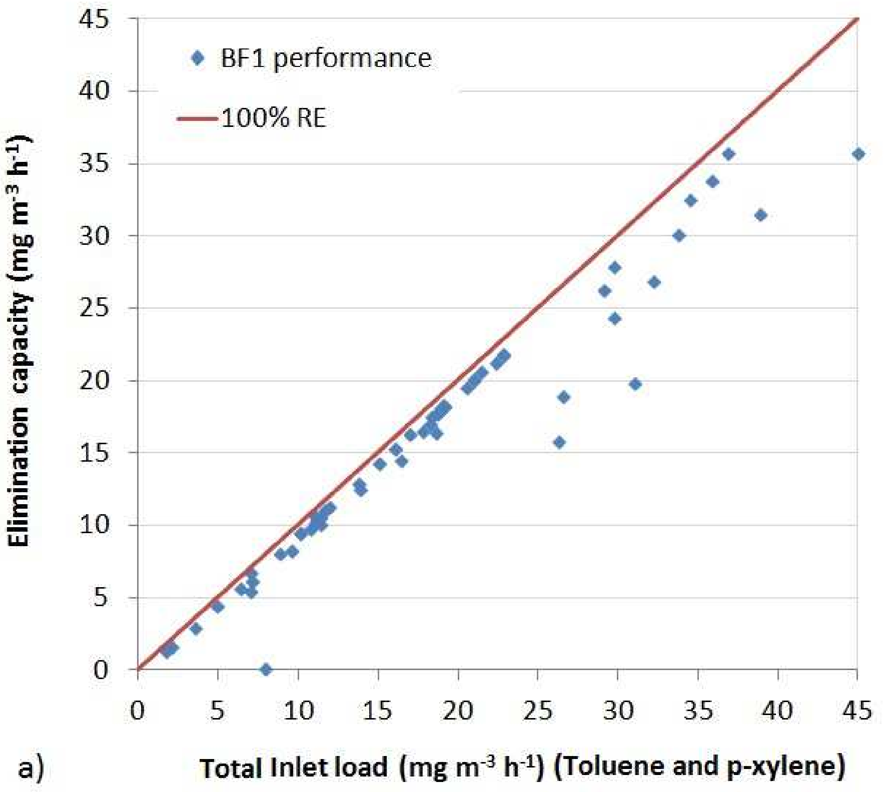
Overall efficiency of the systems

The influence of the total loading rate (both toluene and p-xylene) on elimination capacity (EC) in both systems is shown in Figure 4.25. This figure allows comparing in a more reliable way the performance of both systems as EC takes into account both airflow and biofilter size. The red line indicates 100% removal efficiency of the system and this is reached when EC equals the load (Table 4.3) (Devinny *et al.*, 1999).

As seen in Figure 4.25a, the critical EC for BF was about 22 mg m^{-3} h^{-1}; under this value, mass transfer from gas phase to biofilm was carried out without interferences despite the very low contaminant concentrations in the liquid phase which were calculated based on Henry's law constant reported in Table 4.2 and considering the minimum and maximum concentration values for both pollutants in the gas phase. Results are shown in Table 4.15. These concentrations are indeed low compared to that reported by Roch and Alexander (1997). These authors concluded that a significant mineralization rate and metabolism of toluene could be obtained at a threshold concentration dissolved in water of 0.9 µg L^{-1}, in the presence of other carbon sources and when the medium is inoculated with active bacteria.

For values higher than 25 mg m^{-3} h^{-1} the amount of toluene diffuse in the biofilm start to be limited as can be seen in Figure 4.25a and the microbial activity in turn can decrease (Delhoménie *et al.*, 2002). However, maximum EC for this system cannot be defined because higher loading rates were not tested (in accordance with indoor air concentrations). Figure 4.25b shows a higher EC for compost stage in HS which reached its critical EC near 50 mg m^{-3} h^{-1} and the maximum EC at around 100 mg m^{-3} h^{-1}. At this point, microbial degradation kinetics starts to control biofilter performance (Gallastegui *et al.* 2011b). Considering AC stage higher loading rates were eliminated at 100% and neither critical nor maximum EC were reached.

In Figure 4.26 and 4.27, the elimination capacity as a function of the inlet load is presented for BF and HS, respectively, considering the EBRTs tested for toluene and p-xylene singly. Considering the toluene in the BF, two different EBRT were tested (15 s and 23s). When EBRT was 15 s the EC was slightly reduced but the critical or maximum EC did not appeared. On the contrary, for the p-xylene, critical elimination capacity near to 15 mg m^{-3} h^{-1} was observed for 23s. For the EBRT of 15 s there is not enough data to conclude about the maximum of critical EC. Enclosed data corresponds to values recorded after the starvation period.



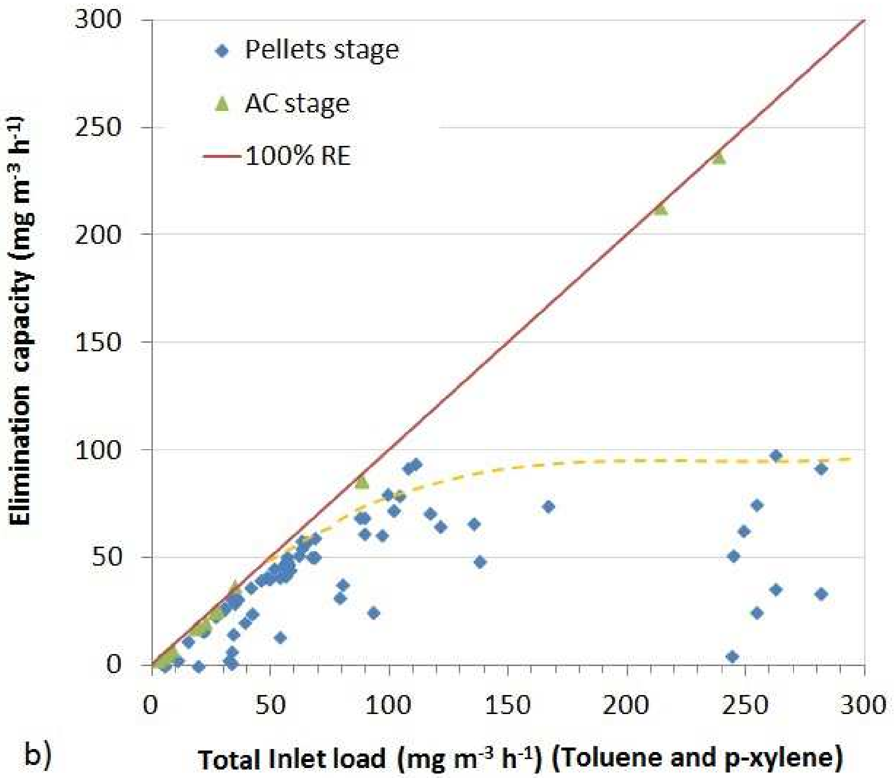
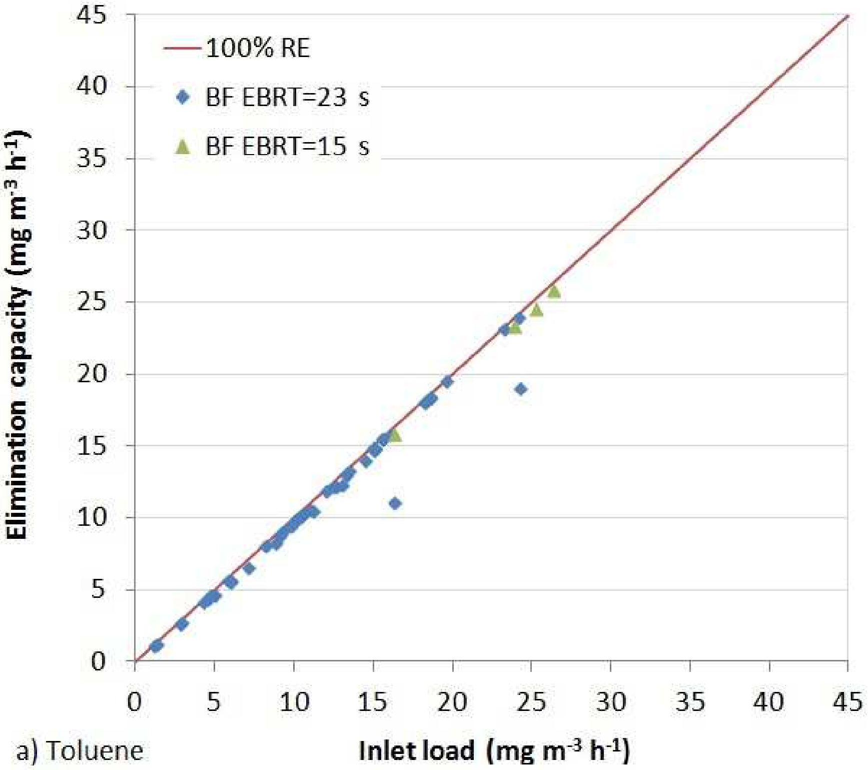
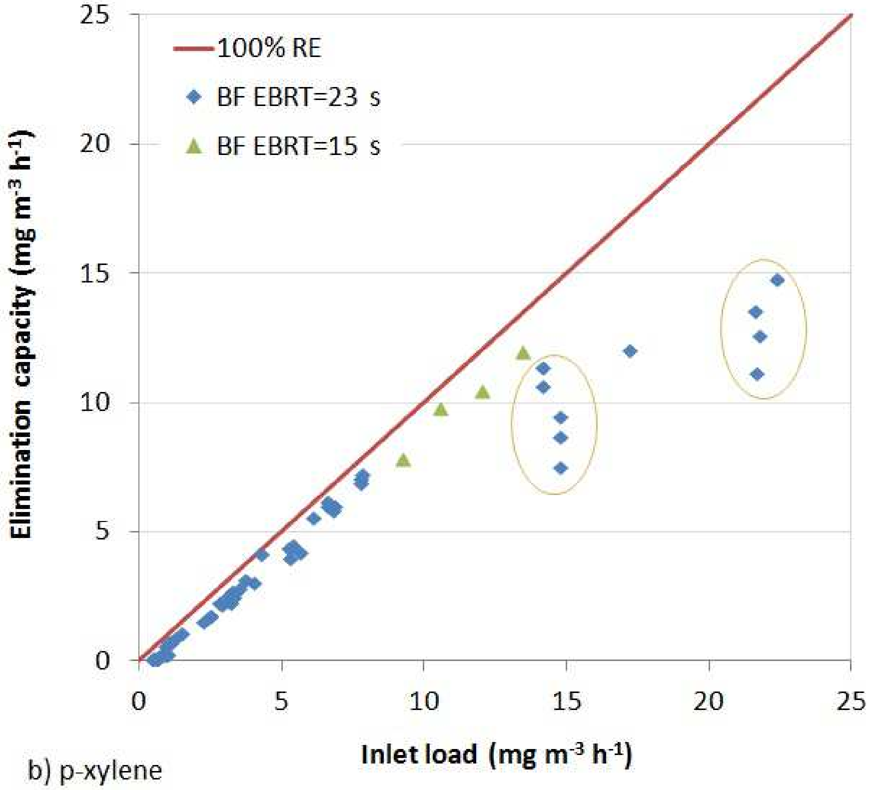


Figure 4.25 Evolution of the elimination capacity vs. inlet load for (a) BF and (b) HS

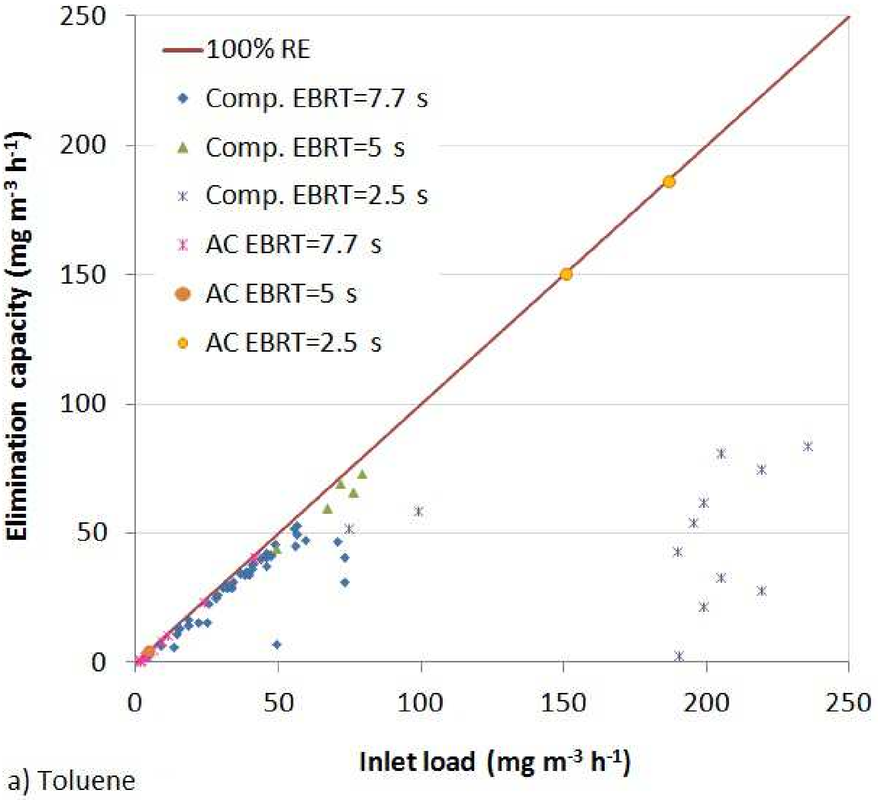


a) Toluene

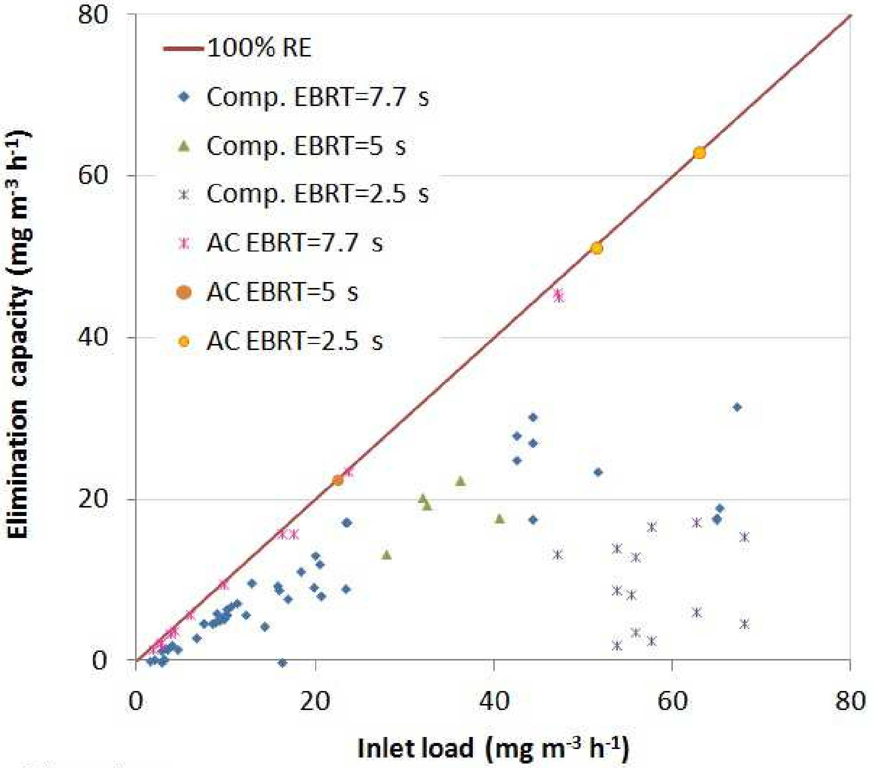


b) p-xylene

Figure 4.26 Elimination capacity vs. inlet load in the BF for the different EBRTs.



a) Toluene



b) p-xylene

Figure 4.27 Elimination capacity vs. inlet load in the HS for the different EBRTs.

Considering the behavior of EC on the HS presented in the Figure 4.27, EBRTs of 2.5 s, 5 s and 7.7 s were tested. At 2.5 s a maximum elimination capacity of 80 and 18 mg m^{-3} h^{-1} for toluene and p-xylene, respectively, were recorded for the compost stage. AC had a much higher EC for these compounds (185 and 62 mg m^{-3} h^{-1} for toluene and p-xylene, respectively). Critical EC at this low EBRT could not be precisely determined but for toluene it could be suggested a value near 50 mg m^{-3} h^{-1}. Regarding the EBRT of 5 s, for the compost stage, a maximum EC of 75 and 22 mg m^{-3} h^{-1} for toluene and p-xylene, respectively, were registered. At an EBRT of 7.7 s the maximum EC for toluene and p-xylene were 52 and 32 mg m^{-3} h^{-1}, in the compost stage and, 40 and 46 mg m^{-3} h^{-1} in the AC stage, respectively. It should be noticed that in the case of the p-xylene, the HS worked over its critical EC during all the experimental time.

Table 4.15 Calculated contaminants' concentrations in the liquid phase.

Compound	H (24.6°C)	C_g (μg m^{-3})		C_l (μg L^{-1})	
		Min	Max	Min	Max
Toluene	0.258	7.443	167.46	0.289	0.649
p-Xylene	0.300	4.288	141.52	0.149	0.472

C_g: pollutant concentration in the gas phase
C_l: pollutant concentration in the liquid phase

Removal efficiencies in HS by stages

Figure 4.28 clarifies the role of different stages in the system HS. The luffa stage did not interfere in the pollutants' removal efficiency. As seen, the stage of activated carbon (AC) played an important role when operational conditions changed over the time. For instance, from day 14 to day 29, EBRT changed twice until it reached a value of 2.5 s, which showed the AC stage was more demanded during this period. Specifically, on day 27, 98% of the toluene removal (Figure 4.28a) and 83% of the p-xylene removal (Figure 4.28b) was assumed by AC stage. From day 130, concentrations of both compounds significantly increased and in day 140, AC was responsible for more than 80% of the toluene removal and about 75% of the p-xylene removal. Overall results indicate that 18% of the toluene and 51% of the p-xylene loads that entered the HS were treated by the AC stage.

Changes in environmental conditions could also influence the adsorption process (cf. 4.2.3.5 and 4.2.3.6). For example, Shin *et al.* (2002) concluded that adsorption capacity of a granular activated carbon for benzene, toluene, and ethylbenzene decreased at relative humidity values over 60% and that this capacity is inversely proportional to the compound concentration. Similarly, Yakout (2014) stated that adsorption increases with the molecular weight of the solute. Other studies had also used the AC together with a biological process (Li *et al.*, 2008; Dorado *et al.*, 2012; Ondarts *et al.*, 2012; Hort *et al.*, 2014; Palau *et al.*, 2015). Dorado *et al.* (2012) used activated carbon as a media of a biofilter. These authors concluded that pollutant adsorption and biodegradation simultaneously took place in the biofilter. They also stated that during the start-up, adsorption phenomenon prevailed over biodegradation.

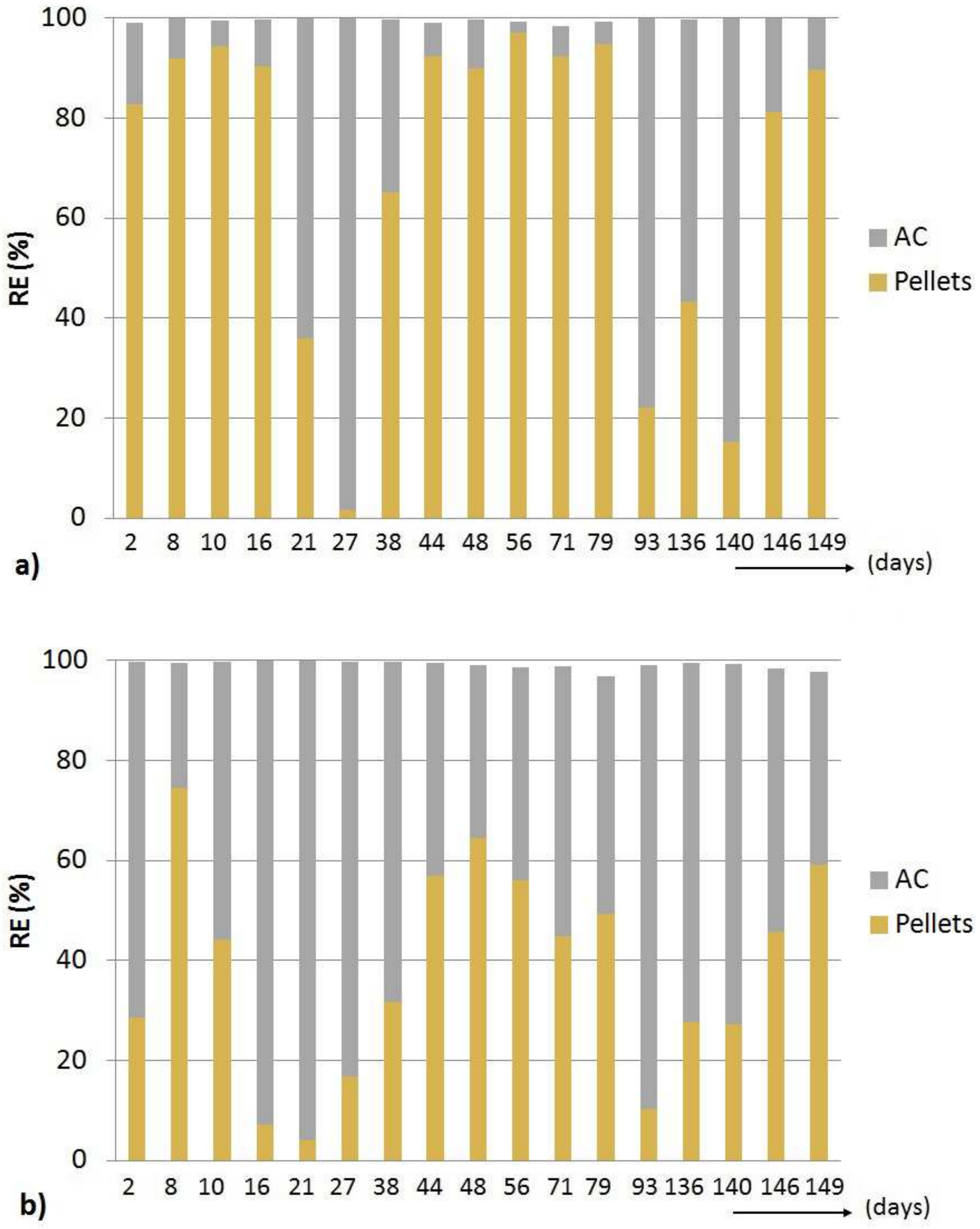


Figure 4.28 Removal efficiency by stages in HS during some specific days for (a) toluene and (b) p-xylene

4.3.3.3. Generation of by-products

Few compounds were identified in the outlet stream of BF and HS by GC/MS analysis. Acetone and acetic acid could be identified in the BF outlet stream (Figure 4.29). The identification of by-products by HS system was not possible during its outlet stream analysis (Figure 4.30); only toluene and p-xylene were identified. The two other peaks on the chromatogram were not identified as probabilities of the possible compounds suggested by the software of the GC/MS were too low. This might be due to the role of AC stage, because the carbon used in this study was chemically impregnated for the preferential adsorption of pollutants like formaldehyde, ketones and alcohols.

Another explanation for the absence of compounds in the outlet stream is because some compounds could be retained on the Nafion® dryer during the pre-concentration sample stage in the analytical process which also applies for BF. As a matter of fact, as Nafion® is strongly acidic due to the presence of the sulfonic acid groups, in addition to water removal, alcohols and certain other organic compounds which can be converted into alcohols such as aldehydes and ketones would be eliminated (Taurkova *et al.*, 2011). These compounds can be acid catalyzed to react with water and undergo a process called enolization (Carey and Sundberg, 2007) to form an alcohol. Further analyses would therefore be needed in order to determine if another kind of by-products can be generated through these systems.

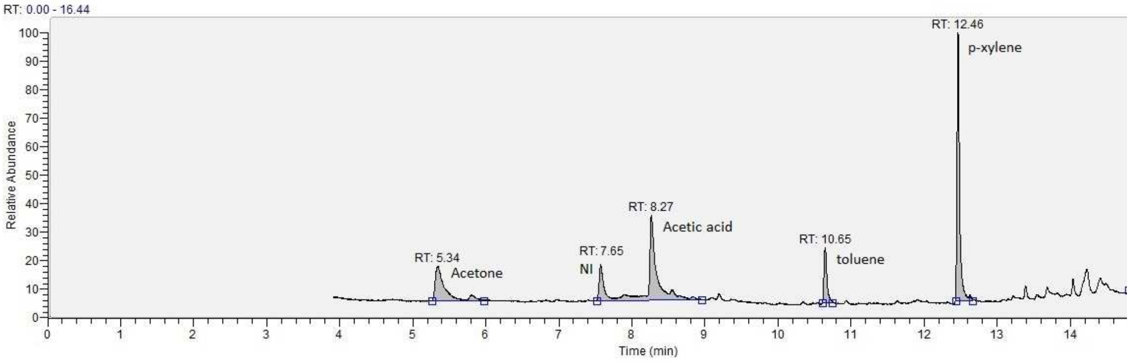


Figure 4.29 Example of chromatogram from the analysis of BF outlet stream.

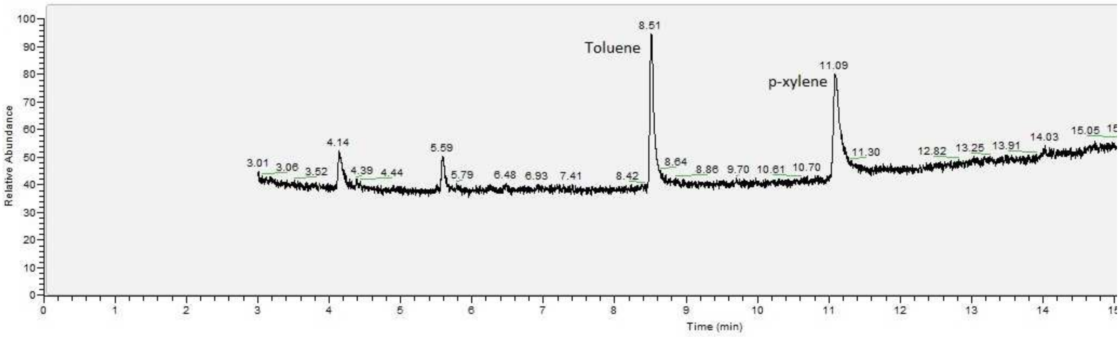


Figure 4.30 Example of chromatogram from the analysis of HS outlet stream.

On the other hand, it is expected to find at the outlet stream higher concentrations of toluene than p-xylene because AC presents higher selectivity towards p-xylene due to the stronger adsorption of p-xylene on the carbon surface and the lower volatility of this compound (Yakout, 2014). Generation of other by-products from similar systems have been reported in other studies. For example, Ondarts *et al.*, (2010) identified acetaldehyde, propanal, acetone, propionic acid, tert-butyl alcohol, ethanol, methanol, and 2-propanol at the outlet stream of a packed biofilter treating butanol, butyl-acetate, toluene, limonene, formaldehyde, undecane, and nitrogen dioxide at indoor concentrations ranging from 32 to 140 µg m^{-3}.

4.3.3.4. Emission of particles

Particle size distribution and concentration in the range of 0.03−10 µm were measured by an ELPI device following an isokinetic sampling ("the sample must be withdrawn from the emission source at a rate such that the velocity and the direction of the gas entering the sampling nozzle is the same as the gas in the duct at the sampling point" (EPA Victoria, 2002)). Nevertheless, according to operational conditions, it is possible to assess if all the emitted particles are taken into account in this measure, or if others can be transported by the flow through the reactor and then be released into the environment.

The maximum particle diameter at which particles can be carried away by the air flow in the BF and HS systems can be determined. First, flow regime is determined by calculation of the Reynolds particle number as follows:

$$\mathrm{Re_p} = \frac{\mathrm{\rho_a\ v\ d_p}}{\mathrm{\mu_a}} = \frac{1 \times 0.021 \times 10 \times 10^{-6}}{1.8 \times 10^{-5}} = 12 \times 10^{-3}$$

where:

$\rho_a = 1.2$ kg m^{-3} (density of the air).

v is the velocity of the fluid (m s^{-1}) in the reactor calculated from the air flow rate Q=10 L min^{-1} and the reactor's diameter D=10 cm

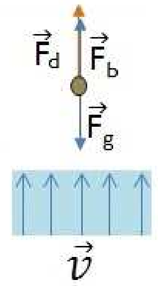
$$v = \frac{4Q}{\pi D^2} = \frac{4 \times 0.010}{\pi \times 0.1^2 \times 60} = 0.021\ m\ s^{-1}$$

d_p is the particle diameter took herein as 10 µm (maximum measured by ELPI device)

$\mu_a = 1.8 \times 10^{-5}$ kg m^{-1} s^{-1} (dynamic viscosity of the air).

As Reynolds number indicates laminar flow (Re<<1), Stokes' law can be used (C_f=24/Re) for establishing the conservation equations of a single spherical particle (ignoring wall effects and interaction with other particles). Gravitational, buoyancy and drag forces act on the particle. From the force balance, it is possible to get the diameter at which a particle reach its buoyancy and can therefore be carried away from the system:

$$\overrightarrow{F_g} = \overrightarrow{F_d} + \overrightarrow{F_b}$$



$$F_g = \rho_p \frac{4}{3}\pi \times \left(\frac{d_p}{2}\right)^3 \times g$$

$$F_b = \rho_a \frac{4}{3}\pi \times \left(\frac{d_p}{2}\right)^3 \times g$$

$$F_d = C_f \times A \times Ec = \frac{24\mu_a}{\rho_a\, d_p\, v} \times \pi \times \left(\frac{d_p}{2}\right)^2 \times \frac{1}{2}\rho_a \times v^2$$

$$d_p = \sqrt{\frac{18 \times v \times \mu_a}{g \times (\rho_p - \rho_a)}} = \sqrt{\frac{18 \times 0.021 \times 1.8 \times 10^{-5}}{9.81 \times (1300 - 1.2)}} = 22\mu m$$

According to these result, particles under 22µm can be released by the systems. Therefore, the ELPI device only measures a fraction of those particles.

Figure 4.31 shows the particle emissions when operating BF and HS systems in the laboratory during one hour. There is a continuous emission particle from both systems despite the very low air velocity (0.021 m s^{-1}) compared to devices installed in real environments to treat the air (offices, hotels, residences) where the air velocities ranged 2 to 8 m s^{-1}. These velocity values are between 95 and 400 times higher than the air velocity of this study, which means that at real conditions, the emission of particles will be greater. Consequently, a filter stage after the treatment system would be necessary in order to reduce the number of particles emitted. Nevertheless, a corresponding increase in pressure drop should be considered.

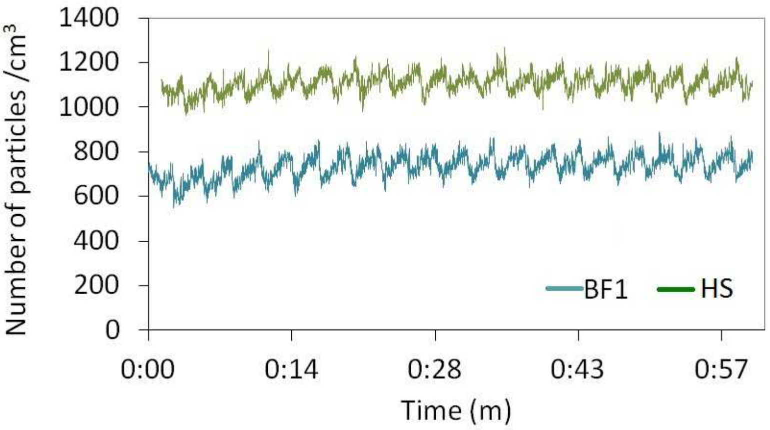


Figure 4.31 Evolution of the emission of particles during one hour of operation of BF and HS system.

In indoor environments, a classification for particle size ranges is proposed by Morawska and Salthamer (2006):

- Coarse particles: particles with aerodynamic diameter larger than 2.5µm
- Fine particles: particles with aerodynamic diameter smaller than 2.5µm
- Ultra-fine particles: particles with aerodynamic diameter smaller than 0.1µm

According to this classification, and as seen on Figure 4.32, most of the emitted particles fixed the ultra-fine group in both systems but the HS emitted a higher quantity. Considering the mass of the emitted particles, Figure 4.33 shows a higher emission of PM_{10} and $PM_{2.5}$ by the HS compared to the BF which could be associated to AC particles (Figure 4.32 and 4.33 are presented in the log-Normal distribution, which represent the number or mass of particles per unit volume of air having diameters in the range of log Dp to log (Dp+d(log Dp).

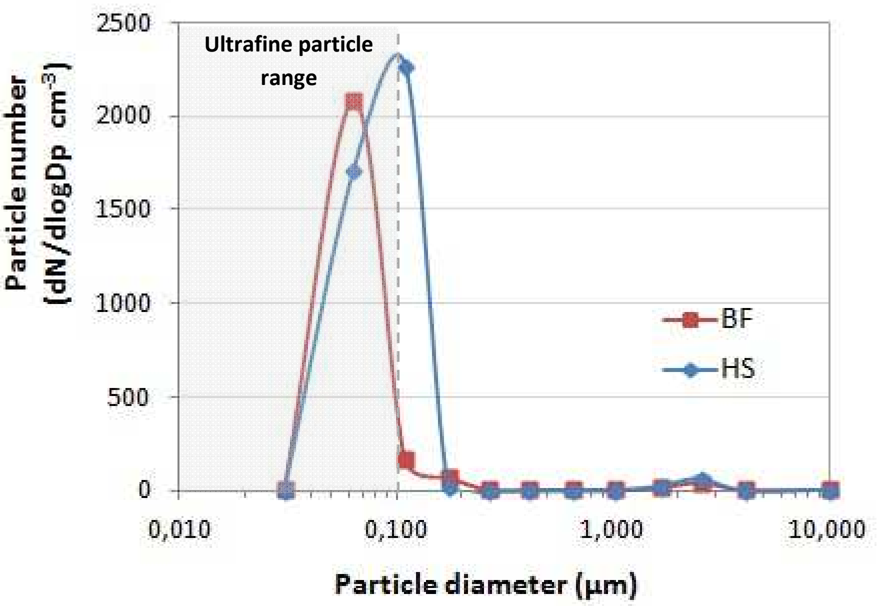


Figure 4.32 Particle size distribution in BF and HS (Dp: particle diameter).

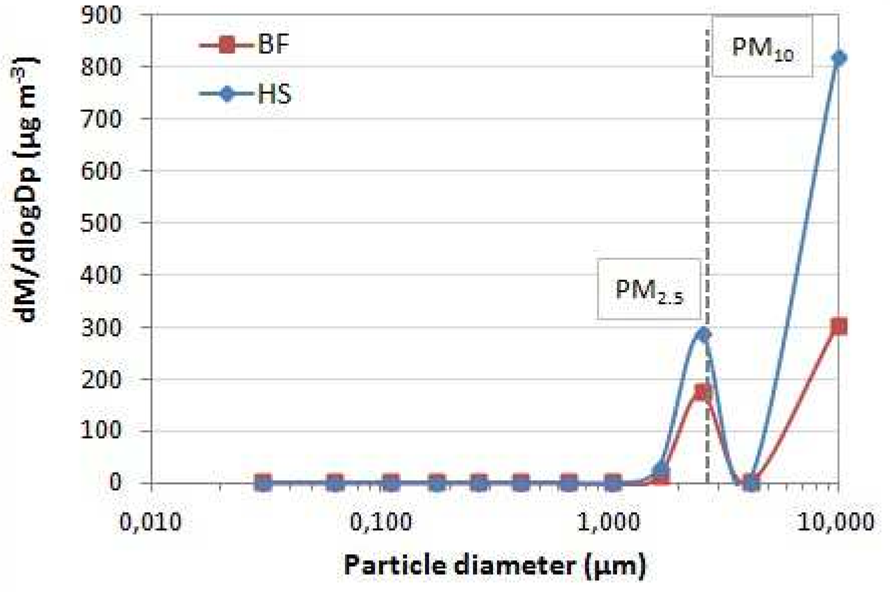


Figure 4.33 Particle mass distribution in BF and HS (Dp: particle diameter).

Average PM_{10} and $PM_{2.5}$ concentrations were 319 μg m^{-3} and 53 μg m^{-3} for the HS, respectively, and 118 μg m^{-3} and 32 μg m^{-3} for the BF, respectively. Mean ultrafine particle number concentrations were 710 and 1095 particles cm^{-3} for the BF and the HS, respectively.

4.4. Conclusions

The overall objective of this chapter has been to compare the efficiency of the biofiltration technology and the hybrid system consisting of the combination of biofiltration and adsorption in the treatment of indoor air pollution. It was proved that even at low concentrations biofiltration was able to achieve high removal efficiencies for the target pollutants. Concerning the biodegradation of the target pollutants, toluene was more easily degradated than p-xylene by biofiltration, reaching high values of removal efficiency throughout the experimental tests. On the other hand, the acclimation period in the biofiltration process was effectively reduced after the inoculation of the compost with an aerobic activated sludge and the exposure of this to higher pollutant concentrations than those found in indoor environments.

The results highlight the potential of the hybrid system as this showed a higher elimination capacity and was the most robust in front of the heterogeneity of indoor pollutants and operational disruptions. Additionally, the AC stage ensured the treatment of bio-by-products which was only detected in a BF system. It would be fruitful to pursue further research about the optimal ratio of biofiltration and adsorption treatment in order to optimize the hybrid system.

The research raises important questions about the particle emissions of both HS and BF systems in indoor environments. This study measured and quantified only in a narrow range of diameter the emitted particles and in a period of time of one hour. Both HS and BF systems released particles in the range of ultrafine particles, $PM_{2.5}$ and PM_{10}. It would thus be of interest to measure particle emissions in a larger size range and in a larger period of time in order to compare with guidelines (values for 24h). These findings also suggest the necessity of implementing a filter at the end of the treatment process in order to reduce particle emissions but, this new stage in the treatment process could increase the pressure drops. Complementary studies should also be focused on controlling air humidity at the outlet of the systems and quantifying the release of microorganisms.

References

Auria R., Aycaguer AC., Devinny JS. 1998. Influence of Water Content on Degradation Rates for Ethanol in Biofiltration. Journal of Air & Waste management Association. 48: 65-70.

Auria R., Frere G., Morales M., Acuña M. E., Revah S. 2000. Influence of Mixing and Water Addition on the Removal Rate of Toluene Vapors in a Biofilter. Biotechnology and Bioengineering. 68(4): 448-455.

Barona A., Elías A., Cano I., Uriarte A., Artetxe J. 2007. Additional Determinations in a Potential SupportMaterial for Toluene Biofiltration: Adsorption and Partition in theNutrient Solution. Chemical and Biochemical Engineering Quarterly. 21 (2): 151–157.

Buekens A. and Zyaykina N.N. 2009. Adsorbents and adsorption processes for pollution control. Encyclopedia of Life Support Systems. Vol. 2.

Carey FA. Sundberg RJ. 2007. Advance organic chemistry. Springer. Fifth edition.

Cheng HH., Hsieh CC., Tsai CH. 2012. Antibacterial and regenerated characteristics of Ag-zeolite for removing bioaerosols in Indoor environment. Aerosol and Air Quality Research. 12 (3): 405-415.

Colman Lerner JE., Sanchez EY., Sambeth JE., Porta AA. 2012. Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina. Atmospheric Environment. 55: 440-447.

Cox HHJ., Doddema HJ., Harder W. 1993. Biological removal of styrene from waste gases using fungi on inert support materials. Biologische Abgasreinigung. 289-299.

Delhoménie MC, Bibeau L, Bredin N, Roy S, Broussau S, Brzezinski R, Kugelmassc JL, Heitz M. 2002. Biofiltration of air contaminated with toluene on a compost-based bed. Advances in Environmental Research. 6(3): 239–254.

Deshusses M. 1997. Biological waste air treatment in biofilters. Current Opinion in Biotechnology. 8: 335-339.

Destaillats H., Maddlena RL., Singer BC., Hodgsona AT., McKone TE. 2008. Indoor pollutants emitted by office equipment: A review of reported data and information needs. Atmospheric Environment. 42 (7): 1371–1388.

Devinny J.S., Deshusses M., Webster T.S. 1999. Biofiltration for Air Pollution Control. Boca Raton, FL, USA: Lewis Publishers.

Devinny J.S., Ramesh J. 2005 Review: A phenomenological review of biofilter models. Chemical Engineering Journal. 113: 187–196.

Dorado AD., Lafuente J., Gabriel D. Gamisans X. 2012. Interaction between sorption and biodegradation in a biofilter packed with activated carbon. Water Science and Technology. 66 (8): 1743-1750.

Dumont E., Andres Y. 2010. Evaluation of innovative packing materials for the biodegradation of H2S: a comparative study. Journal of Chemical Technology and Biotechnology. 85: 429–443.

Dumont E., Andrès Y., Le Cloirec P., Gaudin F. 2008. Evaluation of a new packing material for H2S removed by biofiltration. Biochemical Engineering Journal. 42(2): 120–127.

Elías A., Barona A., Gallastegui G., Rojo N., Gurtubay L. 2010. Preliminary acclimation strategies for successful start-up conventional biofilters. Journal of Air Waste Management Association. 60(8): 959 – 967.

EPA Victoria. 2002. Guidelines for environmental management. A guide to the sampling and analysis of air emissions and air quality. Victoria, Australia. http://www.epa.vic.gov.au/~/media/Publications/440%201.pdf. Accessed 15 September 2015

Estrada JM, Kraakman NJR, Muñoz R and Lebrero R. 2011. A comparative analysis of odour treatment technologies in wastewater treatment plants. Environmental science & technology. 45 (3): 1100–1106.

Estrada JM., Kraakman NJR., Lebrero R., Muñoz R. 2012. A sensitivity analysis of process design parameters, commodity prices and robustness on the economics of odour abatement technologies. Biotechnology Advances. 30: 354–1363.

Gallastegui G., Avalos Ramirez A., Elias A., Jones JP., Heitz M. 2011a. Performance and macrokinetic analysis of biofiltration of toluene and p-xylene mixtures in a conventional biofilter packed with inert material. Bioresource Technology. 102: 7657–7665.

Gallastegui G., Muñoz R., Barona A., Ibarra-Berastegi G., Rojo N., Elías A. 2011b. Evaluating the impact of water supply strategies on para-xylene biodegradation performance in an organic media-based biofilter. Journal of Hazardous Materials. 185(2-3):1019-1026.

Gallastegui G., Barona A., Rojo N., Gurtubay L., Elías A. 2013. Comparative response of two organic biofilters treating ethylbenzene and toluene after prolonged exposure. Process Safety and Environmental Protection. 91: 112–122.

García Martínez J. Pérez Pariente J. 2003. Materiales zeolíticos: síntesis, propiedades y aplicaciones. Publicaciones Universidad de Alicante.

Geiss O, Giannopoulos G, Tirendi S, Barrero-Moreno J, Larsern BR, Kotzias D (2011) The AIRMEX study - VOC measurements in public buildings and schools/kindergartens in eleven European cities: Statistical analysis of the data. Atmospheric Environment 45: 3676-3684.

Gracy S., Hort C., Platel V., Gidas MB. 2006. Volatile Organic Compounds (VOCs) Biofiltration with Two Packing Materials. Environmental Technology. 27(9): 1053-1061.

Guieysse B, Hort C, Platel V, Munoz R, Ondarts M, Revah S (2008) Biological treatment of indoor air for VOC removal: Potential and challenges. Biotechnology Advances 26(5):398-410.

Herrygers, H. Van Langenhove, E. Smet. 2000. Biological treatment of gases polluted by volatile sulfur compounds. Piet Lens, Look Hulshoff Pol (Eds.), Environmental Technologies to Treat Sulfur Compounds, IWA Publishing, London (2000). 281–304.

Hodge DS. Devinny JS. 1995 Modeling removal of air contaminants by biofiltration. Journal of Environmental Engineering. 121 (1): 21-32.

Hort C., Platel V., Sochard S., Luengas Munoz A.T., Ondarts M., Reguer A., Barona A., Elias A. 2014. A hybrid biological process of indoor air treatment for toluene removal. Journal of the Air & Waste Management Association. 64(12). DOI: 10.1080/10962247.2014.958622

Iqbal M., Edyvean RGJ. 2005. Loofa sponge immobilized fungal biosorbent: A robust system for cadmium and other dissolved metal removal from aqueous solution. Chemosphere. 61: 510–518.

Jo WK., Yang CH. 2009. Granular-activated carbon adsorption followed by annular-type photocatalytic system for control of indoor aromatic compounds. Separation and Purification Technology. 66 (3): 430-442.

Jones AP. 1999. Indoor Air Quality and Health. Atmospheric Environment. 33: 4535-4564.

Kandyala R., Raghavendra SPC., Rajasekharan ST. 2010. Xylene: An overview of its health hazards and preventive measures. Journal of Oral and Maxillofacial Pathology 14(1): 1–5.

Kirchner S., Arenes JF., Cochet C., Derbez M., Duboudin C., Elias P., *et al.* 2006. Campagne nationale logement : Etat de la qualité de l'air dans les logements français. Raport final. Observaorite de la Qualité de l'Air Intérieur.

Knaebel K.S. 2004. Adsorbent selection. Adsorption Research Inc. http://adsorption.com/publications/AdsorbentSel1B.pdf

Kostiainen R. 1995. Volatile organic compounds in the indoor air of normal and sick houses. Atmospheric Environment. 29 (6): 693–702.

Kotzias D, Koistinen K, Kephalopulos S, Schlitt C, Carrer P, Maroni M *et al.* (2005) The INDEX project – Critical appraisal of the setting and implementation of indoor exposure limits in the EU. Report. European Commission – Joint Research Centre, Ispra, 51-74.

Le Cloirec P. 2003. Adsorption en traitement de l'air. Techniques de l'Ingénieur.

Lebrero R., Rodríguez E., García-Encina PA., Muñoz R. 2011. A comparative assessment of biofiltration and activated sludge diffusion for odour abatement. Journal of Hazardous Materials. 190: 622–630.

Li L., Wang SB., Feng QC., Liu JX. 2008. Removal of o-xylene from off-gas by a combination of bioreactor and adsorption. Asia-Pacific Journal of Chemical Engineering. 3 (5): 489-496.

Liu Q., Li M., Chen R., Li Z., Qian G., An T., Fu J., Sheng G. 2009. Biofiltration treatment of odors from municipal solid waste treatment plants. Waste Management. 29: 2051-2058.

Lu Y., Liu J., Lu B., Jiang A., Wan C. 2010. Study on the removal of indoor VOCs using biotechnology. Journal of Hazardous Materials. 182: 204–209.

Maestre J.P., Gamisans X., Gabriel D., Lafuente J. 2007. Fungal biofilters for toluene biofiltration: Evaluation of the performance with four packing materials under different operating conditions, Chemosphere. 67: 684–692.

Marin-Ruiz A., Campos-Garcia S., Zavala-Loria J., Solana F., Canedo-Lopez Y. 2009. Assessment of Luffa cylindrica as support in biofilms reactors for the biological treatment of domestic wastewater. Water, Air, Soil and Pollution. 199: 13-21.

Martins V., Cruz Minguillón M., Moreno T., Querol X., de Miguel E., Capdevila M., Centelles S., Lazaridis M. 2015. Deposition of aerosol particles from a subway microenvironment in the human respiratory tract. Journal of Aerosol Science. 90: 103-113.

Mathur AK., Majumder CB., Chatterjee S. 2007. Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media. Journal of Hazardous Materials. 148(1–2): 64–74.

Meunier F., Sun LM. 2003. Adsorption - Aspects théoriques. Techniques de l'Ingénieur, traité génie des procédés, J2730.

Morales M., Hernandez S., Cornabé T., Revah S., Auria R. 2003. Effect of Drying on Biofilter Performance: Modeling and Experimental Approach. Environ. Sci. Technol. 37: 985-992.

Morawska L., Salthammer T. 2006. Indoor Environment: Airborne Particles and Settled Dust. John Wiley & Sons.

Morawska L., Afshari A. Bae GN., Buonanno G. Chao GYH., Hänninen O., Hofmann W., Isaxon C., Jayaratne ER., Pasanen P., Salthammer T., Waring M., Wierzbicka A. 2013. Indoor aerosols: from personal exposure to risk assessment. Indoor Air. 23: 462–487.

Mujumdar AS and Devahastin S. 2011. Fundamental principles of drying. Industrial transfer processes. Departement of Mechanical Engineering. University of Singapore.

Ondarts M., Hort C., Platel V., Sochard S. 2010. Indoor Air Purification by Compost Packed Biofilter. International Journal of Chemical Reactor Engineering. 8: A54.

Ondarts M., Hort C., Sochard S., Platel V., Moynault L., Seby F. 2012. Evaluation of compost and a mixture of compost and activated carbon as biofilter media for the treatment of indoor air pollution. Environmental Technology. 33 (3): 273-284.

Ortiz, I., Revah, S., Auria, R. 2003. Effect of packing material on the biofiltration of benzene, toluene and xylene vapours. Environ. Technol. 24, 263 – 275.

Palau J., Izquierdo M., Marzal P., Martínez-Soria V. 2015. Coupling Adsorption and Biological Technologies for Multicomponent and Fluctuating Volatile Organic Compounds Emissions Abatement: Laboratory-Scale Evaluation and Full-Scale Implementation. Industrial and Engineering Chemistry Research. 54 (6): 1713–1722.

Perreira ML, Graudenz G., Tribess A., Morawska L. (2009) Determination of particle concentration in the breathing zone for four different types of office ventilation systems. Building and Environment, 44(5): 904-911.

Prenafeta-Boldú FX., Guivernau M., Gallastegui G., Viñas M., Sybren de Hoog G., Elías A. 2012. Fungal/bacterial interactions during the biodegradation of TEX hydrocarbons (toluene, ethylbenzene and p-xylene) in gas biofilters operated under xerophilic conditions. FEMS Microbiology Ecology. 80(3): 722-734.

Pujol, Pommier, Debenest, Quintard and Chenu. 2010. Drying in porous media: Equilibrium and non-equilibrium approaches for composting processes. Proceedings of the COMSOL Conference in Paris.

Rahul, Mathur AK., Balomajumder C. 2013. Performance evaluation and model analysis of BTEX contaminated air in corn-cob biofilter system. Bioresource Technology. 133: 166–174.

Rahul, Mathur AK., Balomajumder C. 2011. Biodegradation of Waste Gas containing Mixture of BTEX by B. Sphaericus. Research Journal of Chemical Sciences. 1 (5): 52-60.

Rene ER., Kar S., Krishnan J., Pakshirajan K., López ME., Murthy DVS., Swaminathanf V. 2015. Start-up, performance and optimization of a compost biofilter treating gas-phase mixture of benzene and toluene. Bioresource Technology. 190: 529–535.

Rojo N., Muñoz R., Gallastegui G., Barona A., Gurtubay L., Prenafeta-Bolduc FX., Elias A. 2012. Carbon disulfide biofiltration: Influence of the accumulation of biodegradation products on biomass development. Journal of Chemical Technology and Biotechnology. 87: 764–771.

Romagnoli P., Balducci C., Perilli M., Gherardi M., Gordiani A., Gariazzo C., Gatto MP., Cecinato A. 2014. Indoor PAHs at schools, homes and offices in Rome, Italy. Environment International. 71: 88-93.

Rondeau A., Mandon A., Malhautier L., Poly F., Richaume A. 2012. Biopurification of air containing a low concentration of TEX: comparison of removal efficiency using planted and non-planted biofilters. Journal of Chemical Technology and Biotechnology. 87: 746–750.

Russell A., Brunekreef B. 2009. A focus on particulate matter and health. Environmental science and technology. 43: 4620-4625.

Salthammer T. (2011). Critical evaluation of approaches in setting indoorair quality guidelines and reference values. Chemosphere Volume, 82 (11), 1507–1517.

Sarigiannis D.A., Karakitsios S.P., Gotti A., Liakos I.L., Katsoyiannis A. (2011) Review. Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. Environment International 37: 743–765.

Schlink U., Thiem A., Kohajda T., Richter M., Strebel K. 2010. Quantile regression of indoor air concentrations of volatile organic compounds (VOC). 408 (18): 3840-3851.

Seppänen OA., Fisk W. 2006. Some quantitative relations between indoor environmental quality and work performance or health. HVAC&R Research. 12 (4): 957-973.

Shareefdeen, Z.; Baltzis, B.; Oh, Y-S.; Bartha, R. 1993. Biofiltration of methanol vapor. Biotech. and Bioengineering. 41: 512-524.

Sidheswaran MA., Destaillats H., Sullivan DP., Cohn S., Fisk WJ. 2012. Energy efficient indoor VOC air cleaning with activated carbon fiber (ACF) filters. Building and Environment. 47: 357–367.

Staudinger J., Roberts PV. 2001.A critical compilation of Henry’s law constant temperature dependence relations for organic compounds in dilute aqueous solutions. Chemosphere. 44: 561-576.

Swanson WJ. And Loehr RC. 1997. Biofiltration: Fundamentals, design and operations principles, and applications. Journal of Environmental Engineering.

Taurkova P., Svoboda M., Musil S., Matousek T. 2011. Loss of di- and trimethylarsine on Nafion membrane dryers following hydride generation. J.Anal.At.Spectrom. 26: 220-223.

Wang S., Ang H.M., Tade M.O. (2007). Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. Environment International 33, 694–705

Wargocki P., Wyon DP., Baik YK., Clausen G., Fanger PO. 1999. Perceived air quality, sick building syndrome (SBS) symptoms and productivity in an office with two different pollution loads. Indoor Air 9:165–179.

Weschler CJ., Shields HC., Rainer D. 1990. Concentrations of volatile organic compounds at a building with health and comfort complaints. American Industrial Hygiene Association Journal. 51 (5): 261-268.

World Health Organization (WHO). 1989. Indoor Air Quality: organic pollutants. Report WHO Meeting, Berlin, 23-27 August 1987. EURO Reports and Studies 111. Regional Office for Europe, Copenhagen.

Yakout S.M. 2014. Effect of Molecular Structure on the Adsorption of Soluble Aromatic Hydrocarbons by Activated Carbon . Asian Journal of Chemistry. 26(20): 6891-6894.

Yang RT. 2003. Adsorbents: Fundamentals and applications. John Wiley & Sons. Hoboken, New Jersey.

Yao M., Zhang Q., Hand DW., Perram D. 2009. Adsorption and Regeneration on Activated Carbon Fiber Cloth for Volatile Organic Compounds at Indoor Concentration Levels. Journal of Air & Waste Management Association. 59: 31–36.

Yoon IK., Park CH. 2002. Effects of Gas Flow Rate, Inlet Concentration and Temperature on Biofiltration of Volatile Organic Compounds in a Peat-Packed Biofilter. Journal of Bioscience and Bioengineering. 93 (2): 165-169.

Appendix 4A. Calculation method for the moisture content of the packing material over the time.

The moisture content of the packing material (dry basis) is given by the equation:

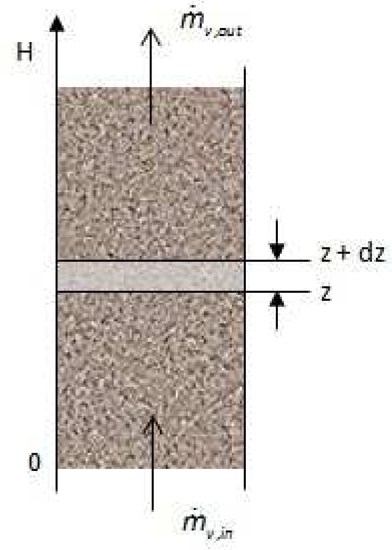
$$X(t) = \frac{m_w(0) - m_{\text{evaporated water}}(t)}{m_{\text{dry.material}}} \qquad \text{(A.1)}$$

where

$m_{\text{evaporated.water}}$ is the mass of evaporated water in the biofilter over the time

$m_w(0)$ is the initial moisture content of the material

$m_{\text{dry.material}}$ is the mass of dry material



The mass of evaporated water for a time dt and a volume dz can be calculated from the mass balance in the vapor phase as follows:

$$d^2 m_v(t) = \dot{m}_{v,in}(z)dt - \dot{m}_{v,out}(z+dz)dt + \dot{\Gamma}_{evap}dt \qquad \text{(A.2)}$$

where

m_v is the mass of the vapour at the instant t

$\dot{m}_{v,in}$ is the inlet mass flow rate of the vapour

$\dot{m}_{v,out}$ is the outlet mass flow rate of the vapour

$\dot{\Gamma}_{evap}$ is the mass flow rate of the vaporisation per extend unit.

Considering the porosity ε of the material homogenous and isotropic, and at constant vapor pressure P_v and temperature T_v inside the biofilter,

$$\rho_v = \frac{MP_v}{RT_v} \simeq constant \qquad \Rightarrow d^2m_v = 0$$
$$V_g = \varepsilon V \simeq constant$$

where

ρ_v is the vapour density

M is the molecular weight

R is the universal gas constant

ε is the porosity of the biofilter

V is the volume of the biofilter

V_g is the gas volume

During *dt*:

$$0 = \dot{m}_{v,\,in}dt - \dot{m}_{v,\,out}dt + \dot{m}_{evap}dt$$

with (A.3) (Instantaneous vaporisation in all the biofilter)

$$\dot{m}_{evap} = \int_{z=0}^{H} \dot{\Gamma} dz$$

Then,

$$dm_{evap} = \dot{m}_{evap}dt = RH_{out}\frac{M}{RT_{out}}P^*_{v,out} - RH_{in}\frac{M}{RT_{in}}P^*_{v,in} \qquad (A.4)$$

where

RH_{out} relative humidity (%) at the outlet of the biofilter

RH_{in} relative humidity (%) at the inlet of the biofilter

$P^*_{v,in}$ and $P^*_{v,out}$ vapour partial pressure at biofilter's inlet and oulet, respectively (Pa).

If $T_{in} = T_{out}$ → $P_{sat,in} = P_{sat,out}$

The evaporated water mass inside the biofilter during *dt* is then,

$$dm_{evap} = (HR_{out} - HR_{in}) \frac{M}{RT} P_{v,sat} dt \qquad \text{(A.5)}$$

The saturation vapour pressure ($P_{v,sat}$) is calculated using Antoine’s law:

$$P_{v,sat}(T) = \exp\left(23{,}1964 - \frac{3816{,}44}{T + 227{,}05}\right) \qquad \text{(A.6)}$$

Finally,

$$x(t) = \frac{1}{m_{dry\ material}} \left[m_v(0) - \int_0^t \dot{m}_{evap} dt \right] \qquad \text{(A.7)}$$

The initial moisture content of the packing material (at t=0) in the BF was 1174.5 g.

Appendix 4B. Link between concentration, ppm and ppb

The ppm as ppb are dimensionless numbers, ratio of particles of a chemical species on the total number of particles in a given volume: 1 part per million (10^{-6}) with respect to the ppm and 1 part per billion (10^{-9}) with respect to the ppb.

$$\text{Concentration: } c = \frac{m}{v}$$

If the number of ppm or ppb is independent of pressure and temperature since it is a proportion of the species concerned from all others (dimensionless), processing of these values in concentration, that involves extensive quantity that is the volume, involves pressure and temperature.

If the chemical species is an ideal gas, it checks

$$p_i V = n_i RT = \frac{m_i}{M_i} RT$$

Where Pi is the partial pressure, n; the number of moles and M, the molar mass of species *i*,

$$c_i = \frac{M_i p_i}{RT} \quad \text{in kg m}^{-3} \text{ (IS)}$$

Link between *ppb* and *µg m*$^{-3}$

If there is 1 molecule of gas *i* per billion molecules of gas, the partial pressure of the gas *i* is:

$$p_i = 10^{-9} p$$

Where p is the total pressure. If there ppb_i gap articles *i* by billions of particles, the partial pressure of the gas *i* is:

$$p_i = 10^{-9} ppb_i \times p$$

$$c_i = 10^{-9} ppb_i M_i \frac{p}{RT} = 120.3 \times 10^{-12} \frac{p}{T} M_i ppb_i$$

The number of *ppb* or *ppm* is independent of pressure and temperature since it is the percentage of presence of a chemical species from all the other chemical species which constitute the gas: if the pressure or temperature changes, the consequences are the same for all species. Instead of the concentration, the mass ratio of the volume depends on the pressure and temperature. Accordingly, the link between *ppb* (*ppm*) and the concentration depends, to a gas, on the pressure and temperature.

Knowing that 1 kg $m^{-3} = 10^6$ mg m^{-3}

$$c_i(\mu g\ m^{-3}) = 120.3 \times 10^{-3}\frac{p}{T}M_i(kg\ mol^{-1})ppm_i$$
$$= 120.3 \times 10^{-6}\frac{p}{T}M_i(g\ mol^{-1})ppm_i$$

Link between *ppm* and *mg m*$^{-3}$

$$p_i = 10^{-6}ppm_i \times p$$

$$c_i = 10^{-6}\ ppm_i\ M_i\frac{p}{RT} = 120.3 \times 10^{-9}\frac{p}{T}M_i\,ppb_i$$

Knowing that 1 kg $m^{-3} = 10^6$ mg m^{-3}

$$c_i(mg\ m^{-3}) = 120.3 \times 10^{-3}\frac{p}{T}M_i(kg\ mol^{-1})ppm_i$$
$$= 120.3 \times 10^{-6}\frac{p}{T}M_i(g\ mol^{-1})ppm_i$$

Relations at 1 atm and 25 ° C

At *p* = 1 atm and T = 25°C = 298 K

$$c_i(\mu g\ m^{-3}) = 40.88 \times 10^{-3}M_i(g\ mol^{-1})ppb_i \leftarrow\rightarrow 24.47c_i(\mu g m^{-3}) = M_i(g\ mol^{-1})ppb_i$$

At atmospheric pressure *p* = 1,013x10^5 Pa:

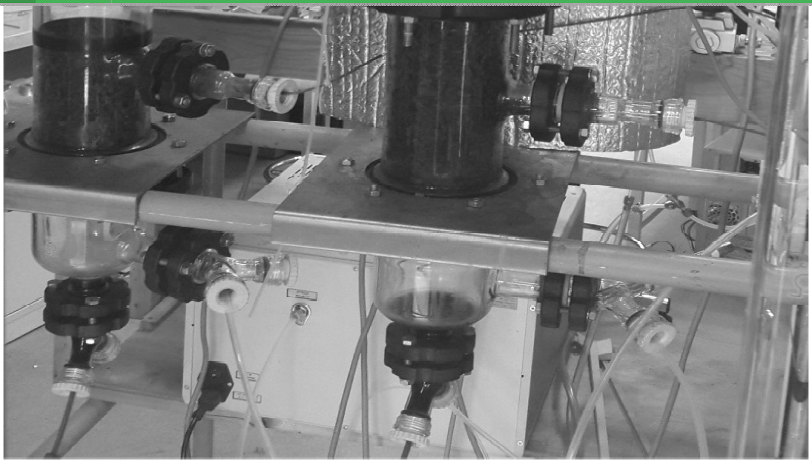
$$c_i(\mu g\ m^{-3}) = \frac{12.18}{T}M_i(g\ mol^{-1})ppb_i$$

In the same way, at p = 1 atm and T = 25°C:

$$c_i(mg\ m^{-3}) = 40.88 \times 10^{-3}M_i(g\ mol^{-1})ppm_i \leftarrow\rightarrow 24.47c_i(mg\ m^{-3}) = ppm_iM_i$$

CHAPTER 5

A HYBRID BIOLOGICAL PROCESS OF INDOOR AIR TREATMENT FOR TOLUENE REMOVAL



5. A HYBRID BIOLOGICAL PROCESS OF INDOOR AIR TREATMENT FOR TOLUENE REMOVAL

5.1. Abstrat

Bioprocesses, such as biofiltration, are commonly used to treat industrial effluents containing volatile organic compounds (VOCs) at low concentrations. Nevertheless, the use of biofiltration for indoor air pollution (IAP) treatment requires adjustments depending on specific indoor environments. Therefore, this study focuses on the convenience of a hybrid biological process for IAP treatment. A biofiltration reactor using a green waste compost was combined with an adsorption column packed with activated carbon (AC). This system treated a toluene-micropolluted effluent (concentration between 17 μg m^{-3} and 52 μg m^{-3}), exhibiting concentration peaks close to 733 μg m^{-3} for a few hours per day. High removal efficiency was obtained despite changes in toluene inlet load (from 4.2×10^{-3} g m^{-3} h^{-1} to 0.20 g m^{-3} h^{-1}), which proves the hybrid system’s effectiveness. In fact, during unexpected concentration changes, the efficiency of the biofilter is greatly decreased, but the adsorption column maintains the high efficiency of the entire process (removal efficiency close to 100%). Moreover, the adsorption column after biofiltration is able to deal 20 with the problem of the emission of particles and/or microorganisms from the biofilter.

5.2. Introduction

Indoor Air Pollution (IAP) is nowadays recognised as a major environmental and health issue. Human exposure studies from U.S. Environmental Protection Agency (EPA) have reported that levels of many pollutants in indoor air may be two to five times, and occasionally, more than 100 times higher than levels found outdoor (U.S. EPA, 2000). It is generally considered that IAP constitutes the main source of exposure to pollution for humans (Jones, 1999; Franklin, 2007) and comparative risk studies performed recently by the EPA and the Science Advisory Board (SAB) have consistently ranked IAP among the top five environmental risks to public health. During recent decades, the prevalence of sick building syndrome (SBS), building related illness (BRI) or multiple chemical sensitivity (MCS) have been reported (Wargocki *et al.*, 1999; Runeson *et al.*, 2006). The importance of indoor air quality is also due to the absolute amount of time that people spend indoors.

Reasons for such a poor quality obviously include many emission sources such as chemical compounds released by building materials or furniture, use of many chemical products, etc. Thus, a wide range of chemical pollutants (Volatile Organic Compounds (VOCs), inorganic pollutants, etc) can be found in indoor air at concentration from less than one µg m^{-3} to few hundred µg m^{-3} (Edwards *et al.*, 2001; Sarrela *et al.*, 2003; Liu *et al.*, 2006; Weisel *et al.*, 2005; Sarigiannis *et al.*, 2011). VOCs concentrations in indoor environments such as home, office, public buildings, and mobile cabins are quite similar. The individual VOC is usually lower than 50 µg m^{-3}; however, total VOCs are much higher.

Consequently, the development of new methods and technologies is necessary to deal efficiently with this poor indoor air quality. Three methods are suggested to control indoor VOCs, namely source control, air cleaning and increase ventilation. Increased ventilation is certainly the easiest technical solution to remove VOCs but is inconsistent with energy savings. Therefore, alternative methods are now studied to control indoor VOCs such as source control and air cleaning. Air cleaning technologies mainly include adsorption onto activated carbon (AC), which is known as a traditional pollution control method to improve transfers pollutants from the gaseous phase to the solid phase. Photocatalytic oxidation (PCO), air ionization, ozone oxidation, or different combined processes seem to be promising technologies for VOCs removal (Wang *et al.*, 2007). Despite very high removal efficiencies are achieved for these processes, they are often limited by selectivity, competition and/or inhibition reactions (Ao *et al.*, 2004a; Ao *et al.*, 2004b). For that reason, other methods for indoor air treatment are now considered by the scientific community.

Bioprocesses, such as biotrickling filters (Lu *et al.*, 2010), biofilters (Wolverton *et al.*, 1984; Wolverton B. C. and Wolverton J. D., 1993; Ondarts *et al.*, 2012) or the use of plants (Orwell *et al.*, 2004; Wang and Zhang, 2011), have already been successfully used to remove VOCs in effluents having constant concentrations. By this technique, microorganisms are generally the main removal agents. Bioprocesses are cost-effective for effluent containing low concentrations of VOCs and constitute a real sustainable technology (no addition of chemical products, waste used as packing medium in the biofilter). However, results from these studies are not always representative of real conditions and some parameters can limit their performance. Indeed, indoor air is characterized by irregular concentrations (presence of pollution peaks) not always easy to treat, and treatments present performances limited by a too high selectivity of the process, by a decrease of removal efficiency due to the lack of water or by the byproducts generation.

Therefore adsorption coupled with biofiltration may enhance the removal of indoor pollutants by facilitating, by sorption phenomenon, the elimination of compounds not easily removable and maintain the efficiency when the feed concentration is suddenly increased. However, because of technological limitations, few studies dealing with adsorption at concentrations close to indoor air pollution levels are available in the literature. Some authors have proposed studies where AC adsorption–desorption columns before the bioprocess may control the effect of pollution peaks (Moe and Li, 2005; Kim *et al.*, 2007; Cai and Sorial, 2009), but always at higher concentrations than those found in indoor air.

Previous works (Ondarts *et al.*, 2012) have shown that the use of biofilter media mixing AC and compost could reach high removal efficiencies (RE) for seven target compounds having different properties in real indoor air conditions (RE upper than 90% for butyl acetate, butanol, formaldehyde, limonene, toluene and undecane). However it was observed that the addition of AC to compost had significant effects such as an increased buffering capacity or adsorption and desorption of trichloroethylene onto this mixed media.

In this present study, we have focused on a hybrid bioprocess based on the combination of a biofilter with an adsorber (AC column) for the treatment of toluene, used here as a target VOC with concentrations close to those found in real indoor air conditions (trace level concentrations). Toluene is a major VOC classified by the European Commission's INDEX strategy report and is almost always present in indoor air at detectable concentrations ranging from a few µg m^{-3} to 358 µg m^{-3} (Sarigiannis *et al.*, 2011; Geiss *et al.*, 2011). Herein, the efficiency of this hybrid biological process was studied with a toluene micro polluted effluent (concentrations between 17 and 52 µg m^{-3}), exhibiting peaks of concentration close to 733 µg m^{-3} during a few hours every day to represent real conditions in indoor air.

5.3. Materials and methods

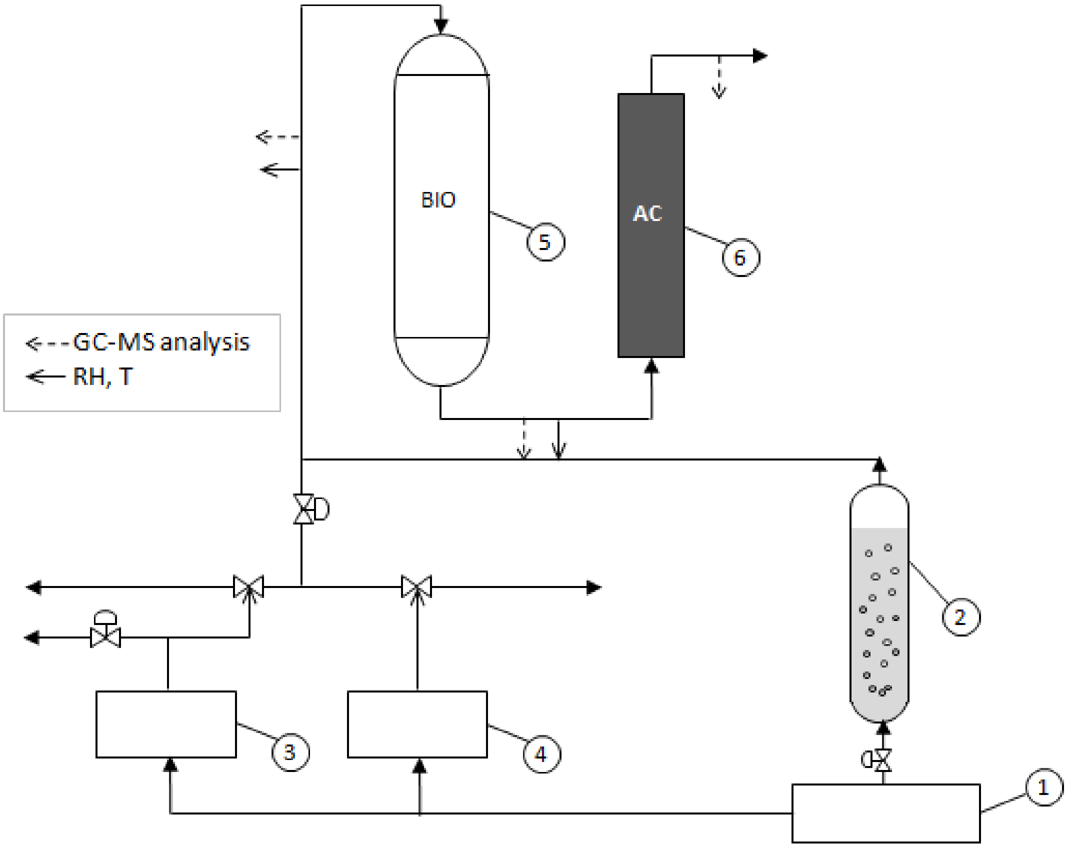
The diagram of the hybrid process combining biofiltration and adsorption is shown in Figure 5.1. The system contains two thermostat chambers where permeation/diffusion tubes generate air containing toluene at constant concentration and enable from time to time to generate toluene concentration peaks. The chambers are feed with zero air from an air generator (Air Liquide). Permeation and diffusion tubes deliver the low and high concentrations of toluene, respectively (from tens to hundreds of µg m^{-3} until some mg m^{-3}).

The volumetric air flow rate feeding the biofiltration/adsorption system is 8.28 L min^{-1}. A dilution flow (0-16.5 L min^{-1}) allows reaching concentrations about ten µg m^{-3} level. The dilution air flow is humidified by passing it through a water bubbler (i.e. pre-humidification). The humidification column has a diameter of 62 mm and an effective height of 30 cm. Relative Humidity (RH) and the temperature are controlled upstream and downstream of the biofilter to monitor the conditions of the biofiltration process (Kimo Instruments and Gefran Coreci, accuracy of 1.5% for RH and 0.3% for temperature measurements). The pre-humidification of the inlet gas stream being not sufficient to provide a good moisture content of the packing material, 90 mL of water is also applied 4 to 5 times a week.

The biofilter consists in a 10 cm diameter pyrex glass column packed with a mature green waste compost completed on 23 cm height. The biofilter was designed according to a low EBRT (Empty Bed Retention Time) of 13 s defined as follows:

$$EBRT = \frac{V_b}{Q_v} \quad (1)$$

where Q_v is the volumetric air flow rate (m^{-3} s) and V_b is the filter bed volume (m^3).



1. zero air generator; 2. bubbler; 3. and 4. thermostated chambers; 5. biofilter; 6. adsorber

Figure 5.1 Representation of the experimental setup

The main parameters studied were the inlet load, IL (g m^{-3} h^{-1}), the elimination capacity, EC (g/m^3/hr) and the removal efficiency, RE (%). EC, RE and IL were determined using the relationships between the toluene inlet concentration, C_{in} (g m^{-3}), the toluene outlet concentration, C_{out} (g m^{-3}), Q_V and V_b:

$$EC = \frac{C_{in} - C_{out}}{V_b} \times Q_V \quad (2)$$

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (3)$$

$$IL = \frac{Q_V \times C_{in}}{V_b} = \frac{C_{in}}{EBRT} \quad (4)$$

The adsorption column, located downstream of the biofilter, has a diameter of 25 mm and is packed with AC over 2.9 cm, getting an EBRT of 0.1 s. The AC used was supplied by Carbio 12 SA (France) and made from coconut shell thermally activated by steam. Its characteristics (given by the supplier or experimentally determined) are: particule size of 1.4 to 4 mm; BET specific surface area of 990 m^2 g^{-1}; microporous volume 0.39 cm^2 g^{-1}; average pore diameter 5.8 Å and pH of 10-11. Mass flow meters are used to control flows (Brooks Instrument, accuracy 1% of the maximal flow rate). A silica gel dryer is put before every flow meter to protect them from humidity. All pipes and connectors are in Teflon or stainless steel to prevent contamination.

5.3.1. Packing material

The packing material was supplied by the Recyclage Organique Mobile Company (specialized engineering in recycling agricultural residues, France). This packing material was mature green waste compost. This compost is a natural support known for its good biofiltration capacity (Ondarts *et al.*, 2012). It naturally provides microorganisms and nutrients. The compost was sieved (2-9 mm) and humidified before the experiment to obtain moisture content between 50% and 60% and a pH between 8 and 9. Ondarts *et al.*, 2012 showed that this compost is a poor adsorbent, with a toluene concentration of 81 µg m^{-3} and a capacity adsorption of 3 10^{-3} µg g^{-1}, which demonstrates that since the concentration of the influent is very low, the amount of pollutant sorbed onto compost cannot be significant.

5.3.2. Experimental conditions

The performance of the hybrid system was studied during 92 days. A micro polluted effluent, containing toluene concentrations from 17 ± 1 µg m^{-3} to 52 ± 3 µg m^{-3} with concentration peaks close to 733 ± 55 µg m^{-3} during a few hours (2-3 h) every day, was treated. The pollutant inlet load varied from 4.2 10^{-3} g m^{-3} h^{-1} to 1.4 10^{-2} g m^{-3} h^{-1} outside the toluene peaks. Concentration peaks were equivalent to 0.20 ± 0.02 g m^{-3} h^{-1}. The average inlet moisture content in the biofilter and in the adsorption column was 53.3 ± 1.5% and 88.2 ± 1.5 %, respectively. The average temperatures were also monitored; their values were 19.6 ± 0.3°C and 18.6 ± 0.3°C for the biofilter and for the adsorber, respectively. The total volumetric air flow rate was maintained at 8.28 L min^{-1}, corresponding to an EBRT of 13.0 ± 0.5 s for the biofilter. For the adsorption column, the EBRT varies between 0.1 and 0.27 s. Operating conditions are summarized in Table 5.1.

Table 5.1 Operation conditions

Parameter	**Biofilter**	**Adsorption column**
Ø (m)	10×10^{-2}	25×10^{3}
H (m)	23×10^{-2}	$29 \times 10^{-3} - 75 \times 10^{-3}$
Media	mature green waste compost	AC C1220 G90 (Carbio12 SA)
EBRT (s)	13 ± 0.5	0.10 - 0.27
Inlet RH_{avg}(%)	53.3 ± 1.5	88.2 ± 1.5
Inlet $Temp._{avg}$ (°C)	19.6 ± 0.3	18.6 ± 0.3

5.3.3. Sampling

To determine efficiency of the system, the toluene concentration was measured upstream and downstream in every step of the process (biofiltration and adsorption) as well as during and outside of concentration toluene peaks with a pre-concentration device (7100A Entech) associated with GC/MS (Trace GC-Trace MS plus, Thermofinnigan) according to the standardized method T0 15, 1999. Physicochemical and biological analyses of the biofilter packing material were performed at the beginning and at the end of the biofiltration (NF V 08-051, 2008).

5.4. Results and discussion

5.4.1. Biofilter treatment

Compared to VOCs treatment using an industrial biofilter, this study for VOCs indoor air treatment is performed using a much lower gas-phase pollutant concentration. The figure 5.2 shows three experimental periods of the biofiltration treatment of toluene at low concentration.

In the first phase, the indigenous microbial population present in the biofilter media was able to treat low concentrations of toluene with removal efficiency (RE) higher than 98% with a lag period of a few hours. However, pollution peaks are only partially treated as shown by a gradual decrease in the RE observed during concentration peaks (dotted line in Figure 5.2). The RE of the biofilter was sensitive to rapid changes in toluene concentration (concentrations between 17 and 733 µg m^{-3}). This could be explained by a progressive reduction of the population density (i.e. aerobic flora) when microorganisms are submitted to constant toluene concentration peaks (Table 5.2).

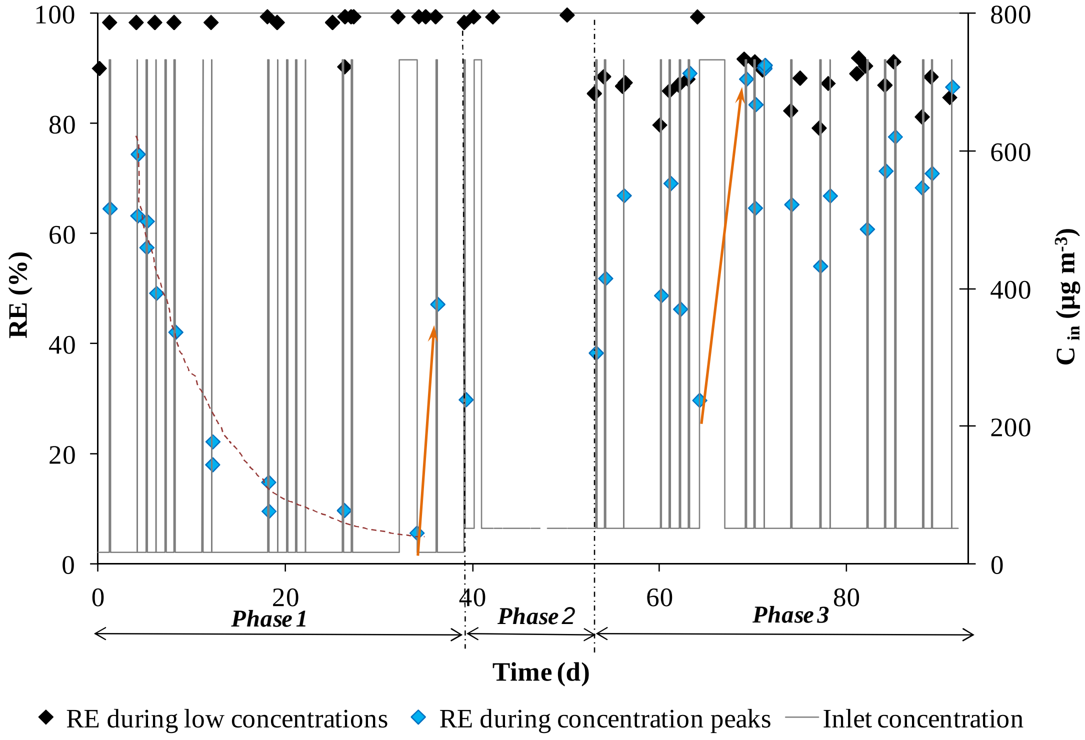


Figure 5.2 Toluene removal efficiency (RE) during and outside peaks.

Table 5.2 Evolution of microorganisms in the biofilter packing material

Microorganisms (CFU g^{-1} of compost)	Time (d) 0	 92
Aerobic flora	1.3 10^7	0.8 10^7
Fungi flora	15 10^3	36 10^3
Anaerobic sulphate reducing bacteria	70	420

The duration of the peaks is not sufficient for them to adapt to this range of concentrations. Longer concentration peaks could be useful for microbial acclimation and it would be then possible to reach better removal efficiency at higher concentrations. Improvements in RE have also been observed at days 34 and 64, after peaks with duration of 47 and 67 hours instead of 2 or 3 hours as usually applied (see arrow in Figure 5.2).

Phase 2 in Figure 5.2 is a period for which changes in permeation and diffusion tubes are necessary. As a consequence, few days (close to 15 days) are required to obtain conditions similar to conditions of phase 1. Then, during the phase 3, the average RE at low concentrations decreases from 98.2 % to 88.2 %. On the contrary, RE is improved during the peaks reaching 72.7 %. This behavior could be the consequence of many factors, including changes in environmental and media conditions as it is shown in Figure 5.3.

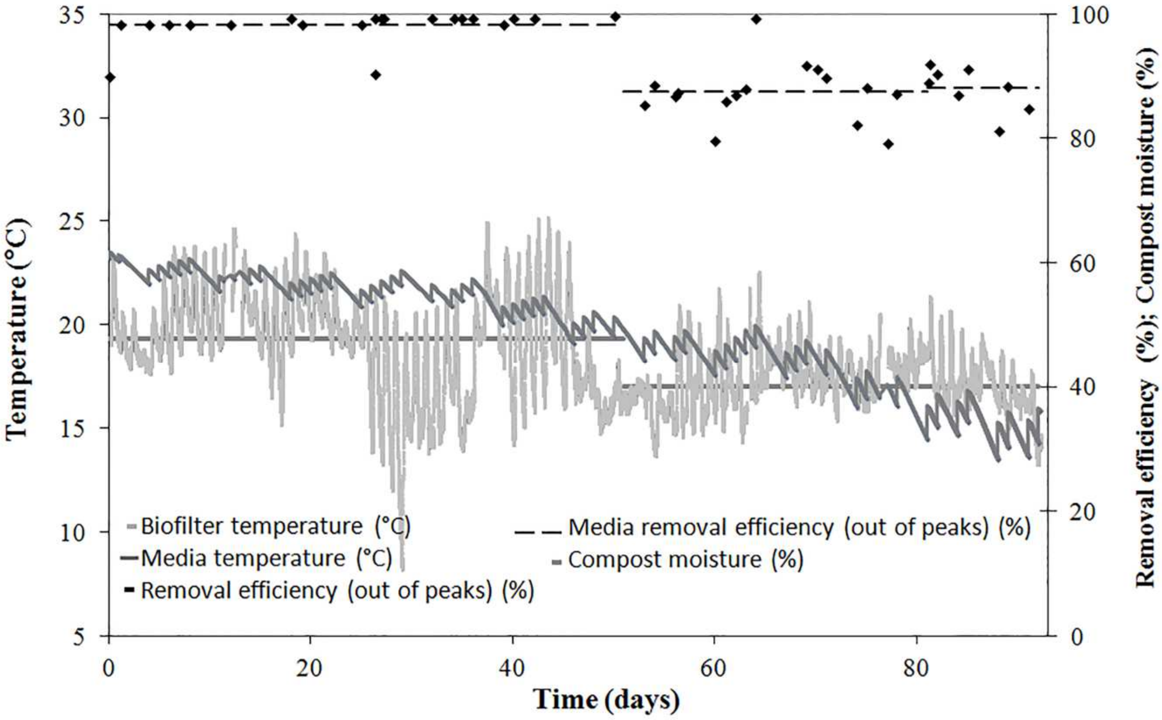


Figure 5.3 Toluene removal efficiency outside concentration peaks versus temperature evolution and compost moisture changes during the experimental study.

According to Figure 5.3, the behavior of RE in biofilter outside the peaks can be compared to the temperature evolution. During the first 45 days (phase 1 and first part of phase 2) , the biofilter worked at an average temperature of 19.3°C which decreases at 17.3°C during the last days of treatment. This temperature change has certainly influenced the RE as suggested by Rahul *et al.*, 2011. They have concluded that removal of BTEX (benzene, toluene, ethylbenzene, xylenes) increases when temperatures increase from 15°C to 25°C following an exponential trend. The role of compost moisture (CM) is also important and has been identified as a key operating parameter determining biofiltration efficiency (Gallastegui *et al.*, 2011). In this study, the compost moisture content shows a loss of 30 % from the beginning until the end of the treatment (Figure 5.3). The influence of CM on the biofiltration RE is well known; it was often observed that media drying is associated with RE degradation for toluene at low (Ondarts *et al.*, 2010) and high concentrations (Morales *et al.*, 2003).

Table 5.2 shows the biological analysis of the compost. 32 % of aerobic bacteria are lost between the initial and the final points of the experimental study. This was also observed by Ondarts *et al.*, 2010 with a higher order of magnitude (loss of 90 % of the initial biomass for an experimental period of 80 days). On the contrary, the fungi population has increased to 240 % which can be considered as normal because of its ability to survive in extreme conditions herein represented by the decrease of CM (Figure 5.3). Microorganisms can be associated with harmful emissions. For example, biofiltration can lead to biological emissions such as fungal spores and mycotoxins even if available studies generally conclude that biological emissions are not significant during treatment using an industrial biofilter (Ottengraph and Konings, 1991; Darlington *et al.*, 2001). These possible biological emissions are even lower in this study where the aerobic bacteria population are in starvation conditions and can be filtered by the adsorption column but this remains to be confirmed later. In addition, a decrease of 80 % in organic nitrogen was observed. This lack of nitrogen can also explain the RE decrease (Gribbins and Loehr, 1998). The presence of anaerobic sulfate reducing bacteria shows the development of anaerobic zones in the biofilter. This could be promoted by the continuous supplying of water which can result in channeling phenomena and compaction of the biofilter media (Gallastegui *et al.*, 2011). Accordingly, when the pollutant concentrations are regular, a packing material having low bioavailability carbon and low biodegradability such as compost based on green waste appears to be a good technological solution for indoor air pollution treatment.

5.4.2. Hybrid biological process (biofiltration/adsorption)

Figure 5.4 shows the biofilter efficiency is greatly decreased during the peaks of concentration but the adsorption column is able to maintain the efficiency of the global process.

During the first 34 days of treatment, the outlet toluene concentrations from adsorption column are not higher to 10.9 µg m^{-3}. Nevertheless, after a long peak of toluene, concentrations up to 93.6 µg m^{-3} were measured and RE decreases from 99.0% to 84.9%. A break on the AC bed can be observed as a consequence of an insufficient residence time in the column. Furthermore, a low desorption from AC is observed after concentration peaks showing an equilibrium change in the adsorption column as a result of the good RE of the biofiltration stage (outlet concentrations of the biofilter are close to zero).

In order to improve efficiency in the adsorption column, the bed of AC was replaced and the EBRT was increased (from 0.1 to 0.27 s) at day 64. After this change, RE ranges between 97.7 % and 99.9 % and desorption is no more observed. Figure 5.5 shows the comparison of toluene EC versus toluene IL obtained in this study and few literature data close to indoor air conditions (Moe *et al.*, 2005; Ondarts *et al.*, 2010; Tang and Hwang, 1997; Abumaizar *et al.*, 1996; Mathur *et al.*, 2007; Oh *et al.*, 2009; Eldon *et al.*, 2005; Delhoménie *et al.*, 2002; Alvarez-Hornos *et al.*, 2008; Lebrero *et al.*, 2012; Gallastegui *et al.*, 2013).

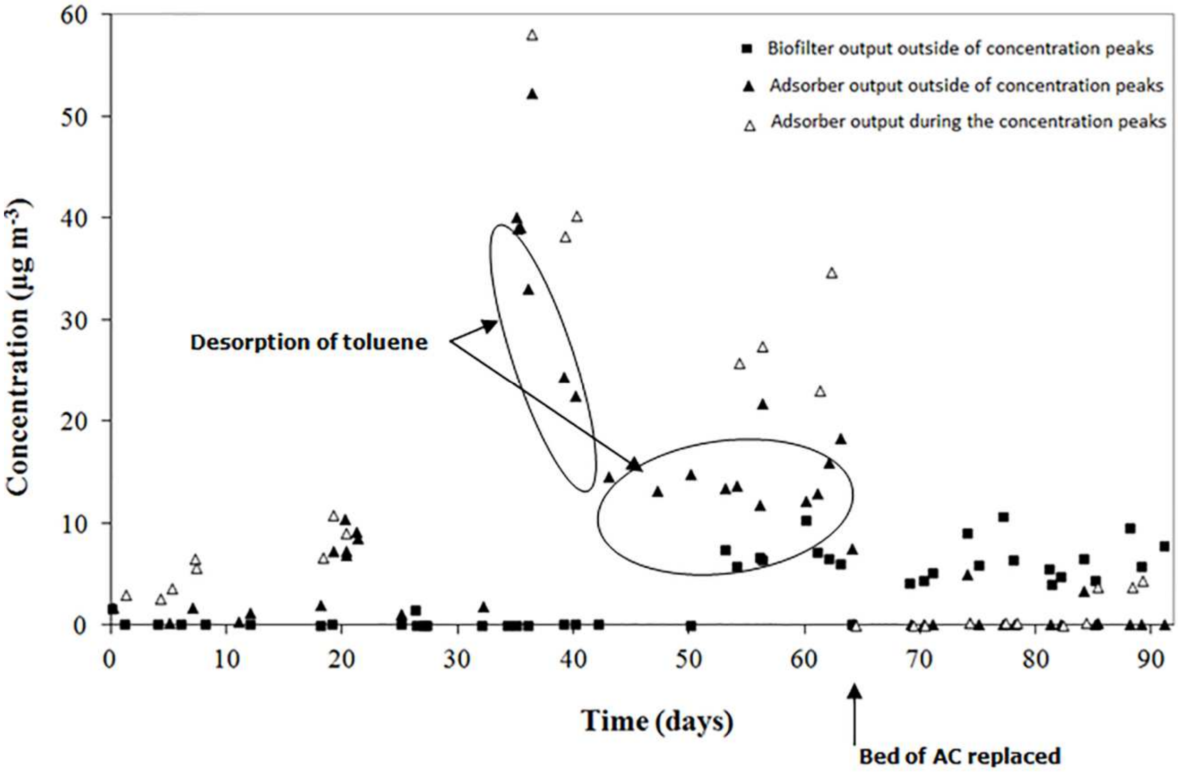


Figure 5.4 Toluene concentrations outside and during peaks of concentration in the hybrid system.

It can be seen from Figure 5.5 that the rapid changes in toluene IL from 4.2 10^{-3} g $m^{-3}h^{-1}$ to 0.20g m^{-3} h^{-1} do not affect the high efficiency (black squares on the 100 % conversion line) of the hybrid biological process. This figure shows that efficiencies obtained in conditions of the field of micro-pollution in indoor air are comparable to those obtained for the treatment of an industrial gaseous effluent (points on the 100% line conversion), even if biological and physico-chemical mechanisms are certainly different and have to be studied later. Accordingly, the adsorption column after biofiltration is therefore able to treat concentration peaks of toluene which was not possible with only biofiltration and certainly avoids the problem of emission of particles and/or microorganisms from the biofilter.

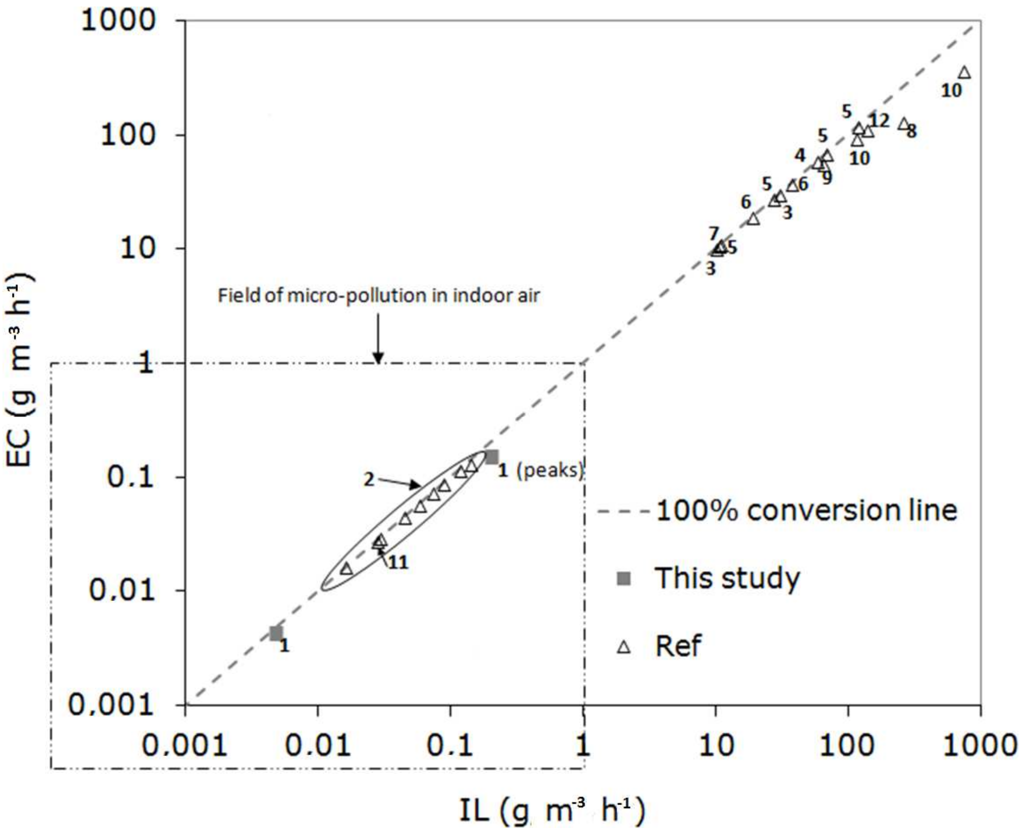


Figure 5.5 Comparison of toluene EC vs. toluene IL from this work (1: black squares) and literature data (triangles ref., 2: Ondarts *et al.*, 2010; 3:Tang and Hwang, 1997; 4: Abumaizar *et al.*, 1996; 5: Mathur *et al.*, 2007; 6: Oh *et al.*, 2009; 7: Moe *et al.*, 2005; 8: Eldon *et al.*, 2005; 9: Delhoménie *et al.*, 2002; 10: Alvarez-Hornos *et al.*, 2008; 11: Lebrero *et al.*, 2012; 12: Gallastegui *et al.*, 2013).

5.5. Design approach

The results obtained from the experiment are analysed in terms of the removal efficiency (RE, percent) of the processes, the inlet mass load of pollutants (IL, g pollutant per m^3 of reactor per min) or the elimination capacity of these pollutants (EC, g pollutant per m^3 of reactor per min), according to the following equations.

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \qquad (1)$$

$$IL = \frac{C_{in} \times Q}{V_f} = \frac{C_{in}}{EBRT} \text{ with } EBRT = \frac{V_f}{Q} \qquad (2)$$

$$EC = \frac{C_{in} - C_{go}}{V_f} \times Q \qquad (3)$$

Where C_{in} and C_{out} are respectively, the inlet concentration of pollutants (g pollutant per m^3) and the outlet pollutant concentration (g pollutant per m^3) of the treatment system, V_f is the volume (m^3) of the filtering element, Q the inlet airflow of micro polluted gas (m^3 per min), and EBRT the empty bed retention time (min).

As regards the design of the coupled processes, the abatement was considered.

$$A = \frac{C_0}{C} \qquad (4)$$

Where C_0 (g pollutant per m^3) is the average concentration of all the pollutants in the room before the treatment system was installed and C (g pollutant per m^3) is the concentration of all the pollutants to be attained after the air has been treated. The inlet airflow (m^3 per min) to be treated by the coupled treatment process is calculated by the following equation used by Guieysse *et al.* (2010).

$$Q = Q_R \times \frac{(A-1)}{RE} \qquad (5)$$

Where Q_R (m^3 per min), is the rate of air exchange in the room.

In France, the Labour Code mandates an airflow renewal rate (Q_R) of 25 $m^3\,h^{-1}$ $person^{-1}$. The air of a room needs to be treated, the room total volume is 30 m^3 (which corresponds to a room of 12 m^2 x 2.5 m) and in which one person is present (Figure 5.6). The average removal efficiency of the system is equal to that obtained with the coupled processes of biofiltration and adsorption (that is, 98 %); with a reduction (A) of 10 (Equation 4), the airflow, as in Equation 5, is of 230 $m^3\,h^{-1}$. In considering an EBRT equal to 20 s and using equation 2, the volume of the filter medium required is 1.3 m^3, which is equivalent to 4 % of the volume of the room.

In this configuration, which treats the entire volume of air exchanged, the coupling of processes can therefore be used when real conditions of air treatment are taken into consideration. However the complexity of the entirety of the elements to be taken into consideration still requires a great deal of study, especially the study of the mechanisms which allow the biomass to be maintained with such weak concentrations of pollutants. The performance of this type of system also needs to be improved, especially when the concentration levels of the pollutants fluctuate. Finally, questions need to be resolved concerning the possible emission of microorganisms and particles (cf. 4.3.3.4).

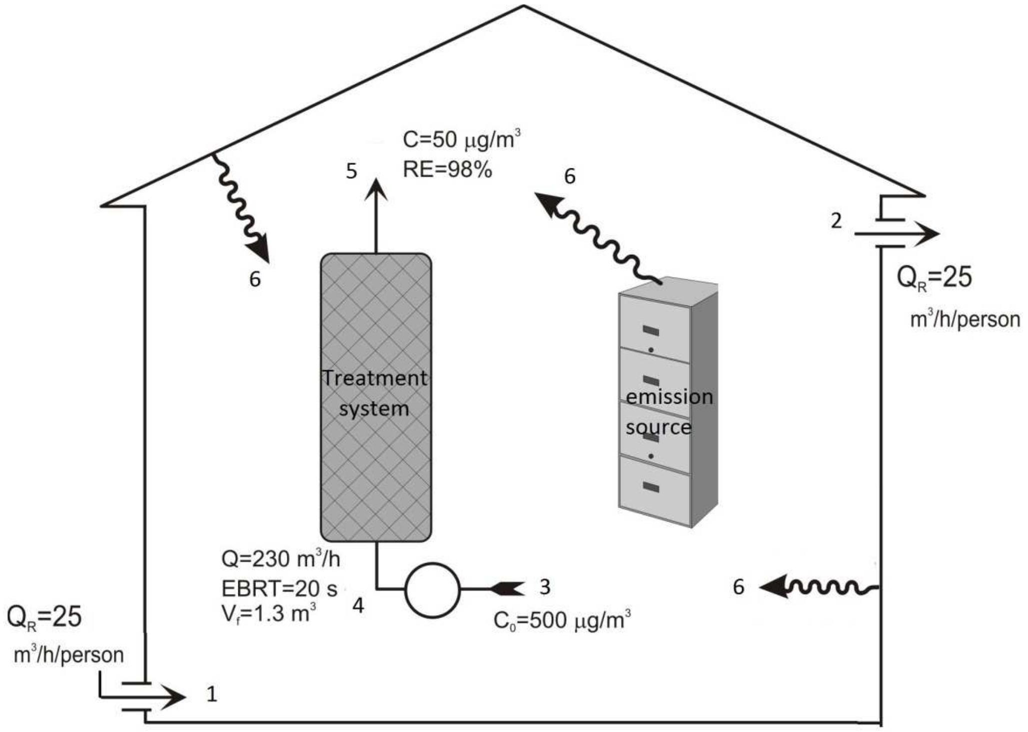


Figure 5.6 Design of the coupled process for the treatment of micro-polluted indoor air (biofiltration/adsorption) in a room: 1) inlet air; 2) outlet air; 3,4) inlet air in the coupled process; 5) outlet air in the coupled process; 6- constant sources of pollutants.

5.6. Conclusions

Biofiltration can efficiently operate at pollutant concentration present in real indoor air conditions (trace level concentration) when inlet load varies from 4.2 10^{-3} to 0.20 g m^{-3} h^{-1} but is sensitive to rapid changes in pollutant inlet load even at very low toluene concentration peaks (733 µg m^{-3}). The adsorption column placed downstream biofiltration is however able to positively manage the toluene concentration peaks.

These results confirm the potential of hybrid biological process such as biofiltration online followed by adsorption as an efficient technology for indoor VOCs treatment. VOCs in indoor air being present under the form of several compounds having very different physico-chemical properties, it is necessary to combine this two processes to remove pollutants by biofiltration that cannot be treated by adsorption and vice versa.

Additional studies need to be performed to suggest the optimal ratio of biofiltration and adsorption treatment. Accordingly, a hybrid biological process appears to be the most promising option to improve the indoor air quality.

References

Abumaizar RJ., Kocher W., Smith EH. 1996. Biofiltration of BTEX contaminated air streams using compost-activated carbon filter media. Journal of Hazardous Materials. 60 (1): 111–126.

Alvarez-Hornos FJ., Gabaldon C., Martinez-Soria V., Marzaland P., Penya-Roja JM. 2008. Biofiltration of toluene in the absence and the presence of ethyl acetate under continuous and intermittent loading. Journal of Chemical Technology and Biotechnology. 83: 643–653.

Ao CH., Lee SC., Yu JZ., Xu JH. 2004a. Photodegradation of formaldehyde by photocatalyst TiO_2: effects on the presences of NO, SO_2 and VOCs. Applied Catalysis. 54: 41–50.

Ao CH., Lee SC., Zou SC., Mak CL. 2004b. Inhibition effect of SO_2 on NOx and VOCs during the photodegradation of synchronous indoor air pollutants at parts per billion (ppb) level by TiO_2. Applied Catalysis B-environment. 49: 187–193.

Cai, Z., Sorial GA. 2009. Treatment of dynamic VOC mixture in a trickling-bed air biofilter integrated with cyclic adsorption/desorption beds. Chemical Engineering Journal. 151: 105–112.

Darlington, A.; Dixon, M. and Mallany, J. 2001. The biofiltration of indoor air II: microbial loading of the indoor space, Quality Solutions Ltd. Naturaire.

Delhoménie MC., Bibeau L., Bredin N., Roy S., Broussau S., Brzezinski R., Kugelmass JL., Heitz M. 2002. Biofiltration of air contaminated with toluene on a compost-based bed, *Adv. Environ. Res*. 6: 239–254.

Edwards, R.D.; Jurvelin, J.; Koistinen, K.; Saarela, K.; Jantunen, M. 2001. VOC source identification from personal and residential indoor, outdoor and workplace microenvironment samples in expolis-helsinki, Finland, *Atmos. Environ.* 35: 4829–4841.

Eldon, R. R.; Murthy, D.V.S.; Swaminathan T. 2005. Performance evaluation of a compost biofilter treating toluene vapours, *Process Biochem*. 40: 2771–2779.

Franklin, P.J. 2007. Indoor air quality and respiratory health of children, *Paediatric. Respi. Reviews.* 8: 281–286.

Gallastegui, G.; Barona, A.; Rojo, N.; Gurtubay, L.; Elías A. 2013. Comparative response of two organic biofilters treating ethylbenzene and toluene after prolonged exposure, *Process Saf. Environ*. 91: 112–122.

Gallastegui, G.; Muñoz, R.; Barona, A.; Ibarra-Berastegi, G.; Rojo, N.; Elías, A. 2011. Evaluating the impact of water supply strategies on *p*-xylene biodegradation performance in an organic media-based biofilter, *J. Hazard. Mater*. 185(2-3): 1019–1026.

Geiss O, Giannopoulos G, Tirendi S, Barrero-Moreno J, Larsen BR, Kotzias D. 2011. The AIRMEX study – VOC measurements in public buildings and schools/kindergartens in eleven European cities: statistical analysis of the data. *Atmos. Environ*. 45: 3676–3684.

Gribbins, M.J.; Loehr, R.C. 1998. Effect of media nitrogen concentration on biofilter performance, *J. Air Waste Manage. Assoc*. 48: 216–226.

Jones, A.P. 1999. Indoor air quality and health, *Atmos. Environ*. 33: 4535–4564.

Kim, D.; Cai, Z.; Sorial, G. A.; Shin, H.; Knaebel K. 2007. Integrated treatment scheme of a biofilter preceded by a two-bed cyclic adsorption unit treating dynamic toluene loading, *Chem. Eng. J*. 130: 45–52.

Lebrero, R.; Rodríguez, E.; Estrada J. M.; García-Encina P. A.; Muñoz, R. 2012. Odor abatement in biotrickling filters: Effect of the EBRT on methyl mercaptan and hydrophobic VOCs removal, *Bioresource Technol*. 109: 38–45.

Liu, W.; Zhang, J.; Zhang, L.; Turpin, B.J.; Weisel, C.P.; Morandi, M.T.; Stock, T.H.; Colome, S.; Korn, L.R. 2006. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States, *Atmos. Environ*. 40: 2202–2214.

Lu, Y.; Liu, J.; Lu, B.; Jiang, A.; Wan, C. 2010. Study on the removal of indoor VOCs using Biotechnology, *J. Hazard. Mater*., 182, 204–209.

Mathur, A.K.; Majumder, C.B.; Chatterjee, S. 2007. Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media, *J. Hazard. Mater*. 48: 64–74.

Method TO-15. 1999. Second edition, U. S. Environmental Protection Agency, USA. Compendium of methods for the determination of toxic organic compounds in ambient air. Determination of volatile organic compounds (VOCs) in air collected in specially - prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS).

Moe, W. M. and Li, C. 2005. A design methodology for activated carbon load equalization systems applied to biofilters treating intermittent toluene loading, *Chem. Eng. J*. 113: 175–185.

Morales, M.; Hernandez, S.; Cornabe, T.; Revah, S.; Auria, R. 2003. Effect of drying on biofilter performance: modelling and experimental approach, *Environ. Sci. Technol*. 37 : 985–992.

NF V 08-051. 2008. Microbiologie des aliments - Dénombrement des microorganismes par comptage des colonies obtenues à 30 degrés Celsius - Méthode de routine.

Oh, D. I.; Song, J. H.; Hwang, S. J.; Kim, J. Y. 2009. Effects of adsorptive properties of biofilter packing materials on toluene removal, *J. Hazard. Mater.* 170: 144–150.

Ondarts, M.; Hort, C.; Platel, V.; Sochard, S. 2010. Indoor air purification by compost packed biofilter, *Int. J. of Chemical Reactor Engineering* 8: Art. n°A54.

Ondarts, M.; Hort, C.; Platel, V.; Reguer, S.; Sochard, S.; Moynault, L. 2010. Developments and new applications of biological gas treatment systems for the removal of micro-pollution in indoor air: study of the design parameters and the associated potential. In: *Proceedings of the 2010 Duke-UAM Conference on biofiltration for Air Pollution Control*, 178–187.

Ondarts, M.; Hort, C.; Sochard, S.; Platel, V.; Moynault, L; Séby, F. 2012. Evaluation of compost and mixture of compost and activated carbon as biofilter media for the treatment of indoor air pollution, *Environ. Technol.* 33: 273–284.

Orwell, R.L.; Wood, R.L.; Tarran, J.; Torpy, F; Burchett, M.D. 2004. Removal of benzene by the indoor plant/substrate microcosm and implications for air quality, *Water Air Soil Poll.* 157: 193–207.

Ottengraf S. P. P. and Konings J. H. G. 1991. Emission of microorganisms from biofilters, *Bioprocess and Biosystems Engineering* 7: 89–96.

Rahul, Mathur, A.K.; Balomajumder, C. 2011. Biodegradation of Waste Gas containing Mixture of BTEX by B. Sphaericus, *Research Journal of Chemical Sciences* 1(5): 52–60.

Runeson, R.; Wahlstedt, K.; Wieslander, G.; Norbäck, D. 2006. Personal and psychosocial factors and symptoms compatible with sick building syndrome in the Swedish workforce, *Indoor Air* 16: 445–453.

Saarela, K.; Tirkkonen, T.; Laine-Ylijoki, J.; Jurvelin, J.; Nieuwenhuijsen, M.J.; Jantunen, M. 2003. Exposure of population and microenvironmental distributions of volatile organic compound concentrations in the Expolis study, *Atmos. Environ*. 37: 5563–5575.

Sarigiannis, D.A.; Karakitsios, S.P.; Gotti, A.; Liakos, I.L; Katsoyiannis, A. 2011. Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk, *Environ. Int*. 37(4): 743–765.

Tang, H.M. and Hwang, S.J. 1997. Transient behavior of the biofilters for toluene removal, *J.* Air Waste Management Association. 47: 1142–1151.

U.S. EPA. 2000. Why is the environment indoors important to US? Washington, DC: Indoor Environment Division, U.S. Environmental Protection Agency. http://www.epa.gov/iaq/pubs/occupgd.html#why%20is%20indoor%20air%20quality%20important.

Wang S., Ang HM., Moses OT. 2007. Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. Environmental International. 33: 694–705.

Wang, Z. and Zhang J.S. 2011. Characterization and performance evaluation of a full-scale activated carbon-based dynamic botanical air filtration system for improving indoor air quality, *Build. Environ.* 46: 758–768.

Wargocki, P.; Wyon, D.P.; Baik, Y.K.; Clausen, G.; Fanger, P.O. 1999. Perceived air quality, sick building syndrome (SBS) symptoms and productivity in an office with two different pollution loads, *Indoor Air* 9: 165–179.

Weisel, C.P.; Zhang, J.; Turpin, B.J.; Morandi, M.T.; Colome, S.; Stock, T.H.; Spektor, D.M. 2005. Relationships of Indoor, Outdoor and Personal Air (RIOPA), part I. collection methods and descriptive analyses, Technical Report, Health Effects Institute.

Wolverton, BC; McDonald, RC; Watkins, J. E. 1984. Foliage plants for removing indoor air pollutants from energy-efficient homes, *Econ. Bot.* 38: 224–8.

Wolverton BC., Wolverton JD. 1993. Plants and soil microorganisms: Removal of formaldehyde, xylene, and ammonia from the indoor environment, *Journal of the Mississippi Academy of Sciences* 38(2): 11–5.

CHAPTER 6

REUSE OF SOIL RECOVERED FROM A CONSTRUCTION SITE AS THE MEDIA IN A BIOLOGICAL SYSTEM FOR THE TREATMENT OF POLLUTED GAS EFFLUENTS, REPRESENTING CONFINED SPACES WITH VEHICULAR TRAFFIC.

6. REUSE OF SOIL RECOVERED FROM A CONSTRUCTION SITE AS THE MEDIA IN A BIOLOGICAL SYSTEM FOR THE TREATMENT OF POLLUTED GAS EFFLUENTS, REPRESENTING CONFINED SPACES WITH VEHICULAR TRAFFIC.

6.1. Introduction

6.1.1. Context

The accumulation of pollutants is the greatest problem in confined spaces with vehicular traffic, such as underground car parks and long tunnels. These pollutants are generated during the combustion process of the internal combustion engine. In 1999, the EPA estimated that vehicles travelling along the highways throughout the United States contributed 29% of total VOC emissions, 34% of total NOx and 51% of total USA CO emissions (McGaughey G. *et al.*, 2004).

Some of the pollutants generated by combustion engines can pose a risk to human health. This is the case with carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs), ozone (a secondary pollutant which is a product of reactions between NO_x and VOCs), formaldehyde and nanoparticles containing Polycyclic Aromatic Hydrocarbons (PAH) which promote bronchial irritation and increase the risk of lung cancer. These latter are intermediates in the formation of soot and were the first carcinogenic compounds to be identified in the atmosphere. Phenanthrene, fluorene and pyrene have been reported frequently as major pollutants in vehicle emissions in tunnels (National Health and Medical Research Council, Australia, 2008).

Other important group in confined spaces with vehicular traffic is the BTEX (benzene, toluene, ethylbenzene and xylenes). About 16% of a typical gasoline blend consists of BTEX compounds. Of the different components contained in gasoline, BTEX compounds are the largest group associated with human-health effects (Lawrence, 2006).

The French Agency for Food, Environmental and Occupational Health and Safety (AFSSET, 2007) assessed the air quality in covered car parks in order to establish the risk that workers are exposed to in such places. Exposure concentrations were measured in four different spaces: a bus station; an underground car park located in a train station; an underground car park located in a shopping centre and a car park reserved for public employees. The compounds to which workers are exposed in these environments are shown in Table 6.1.

Table 6.1 Compounds to which workers are exposed in covered vehicle spaces (AFSSET, 2007)

Type of contaminant	Compound
Inorganics	CO, CO_2, NO, NO_2
Particles	PM10[a], PM2.5[b]
Metals	Lead, cadmium, arsenic, nickel and mercury
VOCs	Benzene, toluene, ethylbenzene, metha and para xylene, ortho xylene, 1,2,4 trimethylbenzene, styrene, heptane and hexane
PAH	Naphtalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene
Aldehydes	Acetaldehyde, formaldehyde, hexaldehyde, propionaldehyde and benzaldehyde

(a) PM10: mass concentration of particles with aerodynamic diameters smaller than 10 µm
(b) PM2.5: mass concentration of particles with aerodynamic diameters smaller than 2.5 µm

6.1.2. Concentration levels

Several studies carried out in different countries have reported concentrations of pollutants commonly found in tunnels and / or covered traffic areas. They are presented in Table 6.2. Concentrations are expressed in the units used in the sources and in ppb (T = 20 °C and P = 1 atm). These compounds are present together with CO and NO_x; for CO, typical values of concentration are between 10 and 40 ppm; NO_x concentrations are generally near 2 ppm.

Table 6.2 Range of concentrations in covered traffic areas

Pollutant	Concentration (µg m^{-3})	Concentration (ppb_v)
Toluene	10.9–1602	2.9– 423 [1–3, 6]
Ethylbenzene	1.3–44.5	0.3 – 10.2 [1, 2, 4-6]
m-, *p*-Xylene	3.3–161	0.8 – 37 [1-6]
o-Xylene	1.3-50.1	0.3 – 11.5 [1, 6]
Formaldehyde	13.8–56.3	11.2 – 45.7 [2–3,6]
Benzene	2.4-682.2	0.8 – 213 [1-4, 6]

[1] Buczynska, A. *et al.* (2005) ; [2] Lee C.M. *et al.* (2011); [3] NHMRC (2008); [4] J. R. Kuykendall (2009); [5] Juszkiewicz, A. and Kijak B. (2004); [6] Na K. (2006).

The compounds listed in Table 6.2 are some of the most abundant in these kind of environments, as their concentration is equivalent to 10% of the VOCs reported in these environments. Although this figure may seem minor, the fact is that hundreds of different VOCs are simultaneously present which makes their contribution significant. The average concentrations of TEX (toluene, ethylbenzene and xylene) and NOx found in underground car parks, in the order of 100 µg m^{-3}, often surpass the values recommended by public authorities (Rondeau, 2012). Moreover, pollutant concentrations in car parks are greater than those found in ambient air. The ratio depends on the pollutant. For instance, in the case of benzene the relation between concentration in a car park and the outdoor concentration was 37 (COPARLY, 2010).

6.1.3. Scope of the study

In this chapter, the reuse of soils recovered from a construction site as the media in a biological system was studied as a request of a company interested in this subject. Two "mixed soils" (that will be called in the present study as Soil-1 and Soil-2) were selected, characterized, and subjected to an acclimation period. Then, the feasibility of using this kind of material as support in a biofilter was analyzed. A polluted air containing toluene, ethylbenzene and p-xylene was treated in the biological system. There are no previous publications in which the possibility of simultaneously treating these compounds with mixed soil generated by construction sites was analysed.

6.2. Materials and methods

6.2.1. Design, installation and start up

In this study, two bioreactors were proposed: BF1 and BF2, packed with Soil-1 and Soil-2, respectively. These reactors operated in parallel as shown in Figure 6.1.

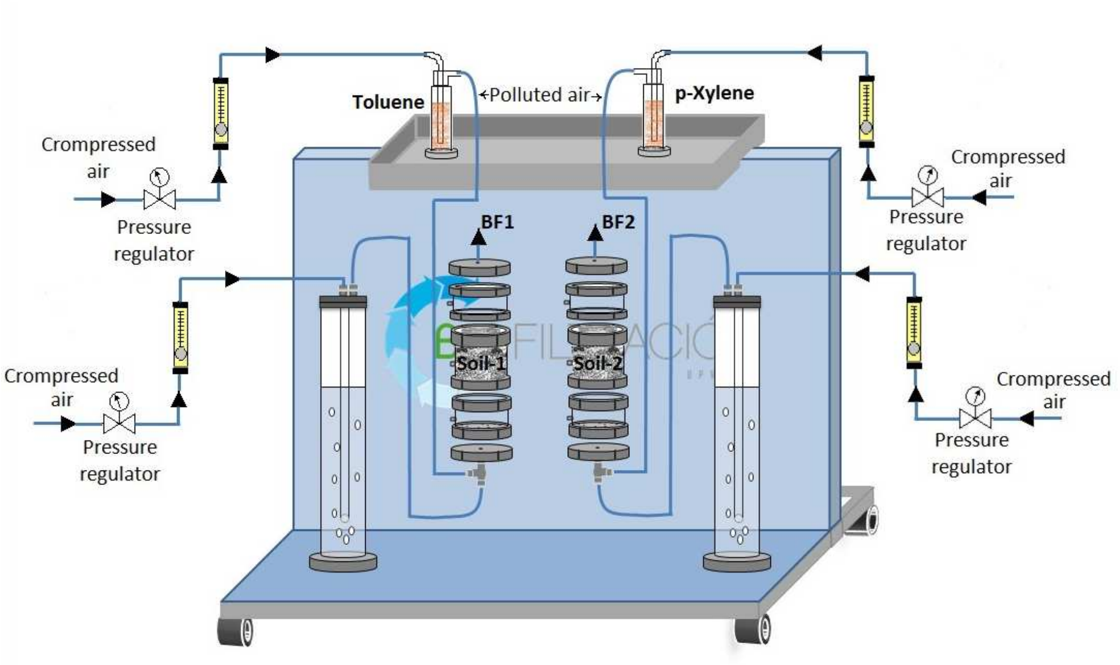


Figure 6.1 Schema of the pilot plan design.

An air stream generated by a compressor is divided into two parts: one stream to produce moist air (main stream) and a second air stream to produce contaminated air (secondary current). Both streams are regulated by rotameters. These rotameters are placed before the humidification column (in the case of the main stream) or before bubblers containing the contaminants (in the case of the secondary current). In the case of the main stream, the air is introduced into a humidifier with deionized water (liquid depth between 30 and 45 cm) in order to saturate the air before it enters the bioreactors.

In the case of the secondary air stream, the stream should be subdivided so that there are as many secondary currents as the number of pollutants. Each of these sub-currents passes through the corresponding rotameter which is adjusted to reach the desired concentration of the pollutant. Finally, the secondary currents are reunited into a single flow stream along with the humid, clean air at the biofilter inlet feeding the system.

Samples are taken at each stage of the system so that changes in pollutant concentration are registered throughout the entire height of the biofilter and, therefore the overall process efficiency is calculated. Operating conditions are summarized in Table 6.3.

Microorganisms need to be provided with nitrogen, phosphorous, potassium and other dietary elements to keep their development and activity. 100 mL of a nutrient solution containing these elements were added to the system once a week. The composition of this nutrient solution has been previously reported by Elías *et al.* (2010).This solution was homogeneously distributed drop by drop on the top of the system in order favour its penetration in all the media. Optimum moisture content was fixed at 20%.

Table 6.3 Operating conditions used in this study.

Dimension	Pollutant	Concentration (ppm)	Flow mode	Air Flow (L min^{-1})	EBRT (s)	T (°C)
Module 15 cm (D) x 20 cm (H)	Toluene *p*-Xylene Ethylbenzene	< 120	Up flow	0–1	80–180	15-25

6.2.2. Soil selection and characterization

The application of biological processes to TEX compounds and other organic compounds, including aliphatic, aromatic, halogen, sulfur and nitrogen hydrocarbons, terpenes, alcohols, aldehydes, etc., has been extensively studied using organic materials (peat, compost, wood, etc.) in the treatment of a large range of pollutant concentrations (1-5 g m^{-3}). The organic nature of a packing material implies the presence of microorganisms that may specialize in metabolizing or degrading pollutants. Media properties such as pH level, particle size, porosity, moisture-holding capacity, organic matter content, ion exchange capacity, etc., should favour metabolic activity in the microorganisms and generate the biodegradation of contaminants.

Accordingly, two soils were proposed for use as support for a biological system. These soils were recovered from a construction site in order to recycle waste material. The composition and character of the selected soils were established with a complete substrate characterization. This characterization together with the results obtained during continuous biofiltration of polluted gas, have the purpose of evaluating the most important and decisive factors influencing the selection process of the soil.

Table 6.4 shows how most of the parameters used in the literature are related to the characteristics of the support which prevent soil-compaction, contraction and / or aggregation. In some cases, due to their small particle size, the option of mixing the organic material (compost from different sources, peat, compost, etc.) with other natural materials (wood chips, bagasse, etc.) provides increased manageability and delays the compaction process.

6.2.3. Determination of the soils' wettability

Wettability is a measure of the how easily a soil can be re-wet once it has dried out. Water distribution may not be uniform during irrigation after a period of drying, because water could be stored in a few large pores, whereas many small pores can remain dry. It is important to keep in mind that microorganisms need water for its activity which is obtained from water retained by the packing material. The more hydrophobic is a support, the harder it will recover microbial activity after a period of dryness (Devinny *et al.*, 1999). To determine this parameter in soils after a period of drying, an experimental setup was designed as shown in Figure 6.2.

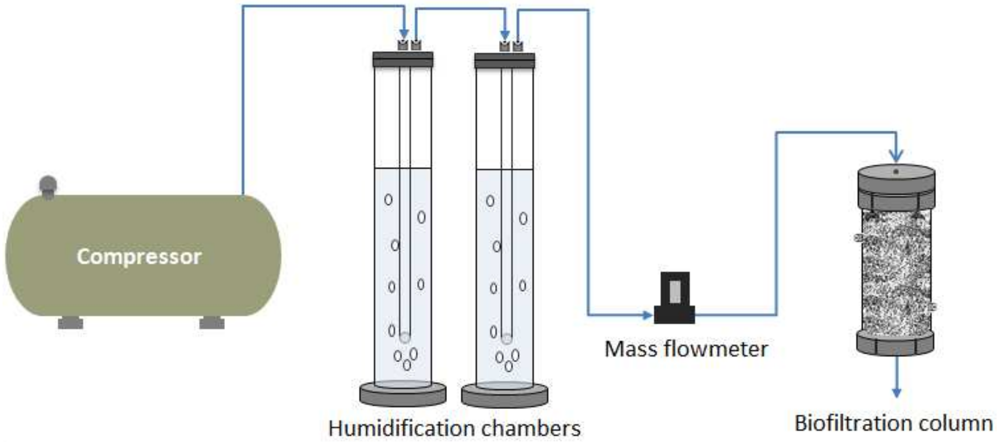


Figure 6.2 Experimental setup for wettability test.

Compressed air is humidified in a bubbler water column. The wet air passes through a biofiltration column which consists of a PVC cylinder 7 cm of height and diameter of 10 cm. 300 g of dry soil (>24 h at 105 °C) are placed in this column. A flow rate of 1 L min^{-1} of saturated air goes through the system. The evolution of soils' moisture content is followed by weighing the corresponding column over the time.

Table 6.4 Parameters of organic materials used as support in bio-treatment

Ref.	Material	Particle size (mm)	Moisture (%)	pH	Density (g m^{-3})	Ratio C/N	Organic carbon (% dried mass)	Organic matter (%)	N/P/K	Porosity (%)
Kaosol, 2012	Manure fertilizer	-	2.7	8.60	0.23	5.50	13.10	22.70	2.37/0.78/0.91	-
Hwang, 2007	Food waste compost	-	40.8	9.25	0.40	-	-	-	2.99/-/-	-
Sattler, 2009	Gardening waste compost	1.5	50–55	5.7–6.1	0.5	-	-	-	-	91
Yang, 2011	Peat	0.2–0.8 (54%)	39.5–52.1	4.3	0.158	55	28.0	49.9	-	66.8
Yang, 2011	White wood mulch	0.2–0.8 (44%)	39.5–52.1	7.0	0.170	37	21.9	40.8	-	73.2
Ondarts, 2012	Green waste compost	4–7	55	-	0.433	-	-	-	-	-
Gutierrez, 2014	Pruning waste	-	55	7.0	0.158	-	-	-	-	85

6.2.4. Surface area

Specific surface area determines the water holding capacity which is related to the transfer of contaminants, nutrients and oxygen across the biofilm (Devinny *et al.*, 1999). It can be defined as the ratio between the absolute surface area A of a solid and its mass (unit: $m^2\ g^{-1}$). The surface area includes all parts of accessible inner surfaces (mainly pore wall surfaces). To determine this parameter, the sample is previously dried and outgassed by heating under vacuum at 300 °C for 3 h, and then, known amounts of adsorptive gas are admitted stepwise. Adsorption and desorption isotherms of N_2 at -196 °C are determined by using a Autosorb®-1-C / TCD equipment (Quantachrome, USA).

6.2.5. Pressure drop (ΔP) study

Pressure drop in a biofilter is indicative of an increase in airflow resistance through the bed which could be is related to bed compaction (Delhoménie and Heitz, 2005). Large pressure drops involve higher power consumption and, accordingly, the operating costs also increase. Even when a pressure drop is not detected, channeling incidents can occur through the bed promoting the inactivation of part of the biofilter and deterioration of the overall performance. Therefore, pressure drop across the bed limits the continuous operation of a biofilter system. Typical pressure drop values in pilot plants vary from 15 to 460 Pa m^{-1} during long term operation (Maestre *et al.*, 2007).

A trial was designed to determine the pressure loss generated by bed compaction. This design considers the effect of moisture in the pressure loss as some authors found that excessive water content on the surface of the packing material can contribute to the agglutination of small material particles that can restrict the gas flow through the bed (Son, 2008; Delhoménie and Heitz, 2005). Similar trials were implemented by Dorado *et al.* (2010) which studied the pressure drop of different packing materials when they were wet and dry (e.g. coconut fiber, compost, lava rock, polyurethane foam, etc.). These authors found a maximum pressure drop, for all materials both dry and wet conditions, of 3.5 cm of water m^{-1}. However, they detected higher pressure drops during wet conditions (between 5 and 30% more important than in dry conditions) due to the water retained on the surface material. This was more important in the case of highly porous materials and with high water retentivity values.

Pressure drop was determined for Soil-1 and Soil-2 in xerophytic (extreme dryness) and flooding conditions. 500 g of packing material (only the particles with a size between 2 and 5 mm) were used. Three modules (diameter 10 cm and height 10 cm) were implemented as shown in Figure 6.3. Middle module contained the packing material and upper and down modules are used to measure pressure drop. The air was saturated in a humidification column and the flow rate at the entrance of the system was regulated at 15 L min^{-1} by a rotameter.

Test in xerophytic conditions.

The material was dried at 105°C for 24h and was introduced in the middle module. Feed of the systems was in the downflow mode the 40 days and then changed to upflow mode. The equipment used in the control of this parameter was the Testo 315-2, which has a measuring range of 0-40 hPa with an accuracy of 0.01 hPa.

Test in controlled flooding conditions.

After xerophytic conditions, the air flow was stopped and middle module was weighted and irrigated with water until flooding the packing material. Then, after 15 min passed, the module was strained during 20 min and weighted again. Afterwards, air flow was reestablished in upflow mode to avoid lixiviation.

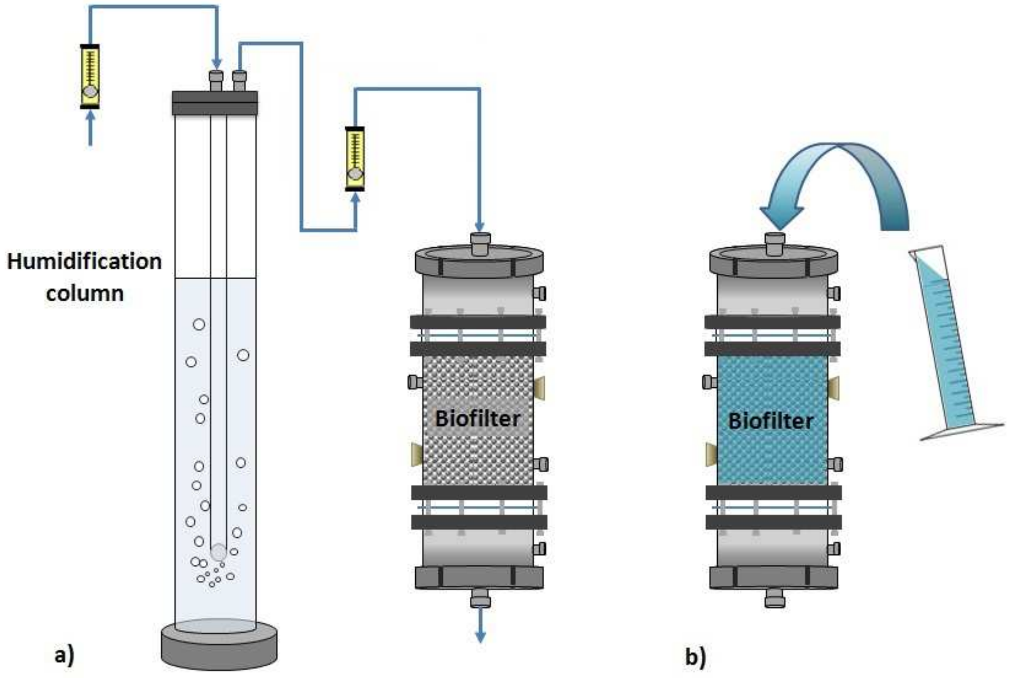


Figure 6.3 Set up of the system to measure pressure drop: a) test xerophytic conditions; b) flooding conditions

6.2.6. Adsorption study

The removal efficiency of the pollutants in biofilters is highly influenced by the adsorption capacity of the packing material. In the present study, adsorption capacity of both soils (Soil-1 and Soil-2) was determined in dry conditions for the packing materials and the inlet stream (without humidification). 850 g of dry material (24h, 105°C) were taken to carry out this test. Dry inlet air stream was obtained by means of a silica gel column placed before the biofilter which ensured an inlet relative humidity below 10% during all the experimental time. Contaminant concentration was continuously measured by GC. The experimental time was 48 h. Flow rate was fixed at 0.6 L min^{-1} (EBRT= 90 s). Temperature was maintained at 25°C and the pressure was 1011 mbar. Toluene was chosen as the target pollutant at concentrations in the range of 250 to 2700 ppm. The soil sample was always the same for all the tests in order to avoid changes in material composition. Consequently, after each adsorption test, a non-polluted dry air stream was passed through the bed in order to remove the toluene from the soils. The concentration was continuously monitored by gas chromatography until no signal was observed (during at least 24 hours). Figure 6.4 shows the experimental setup for this trial.

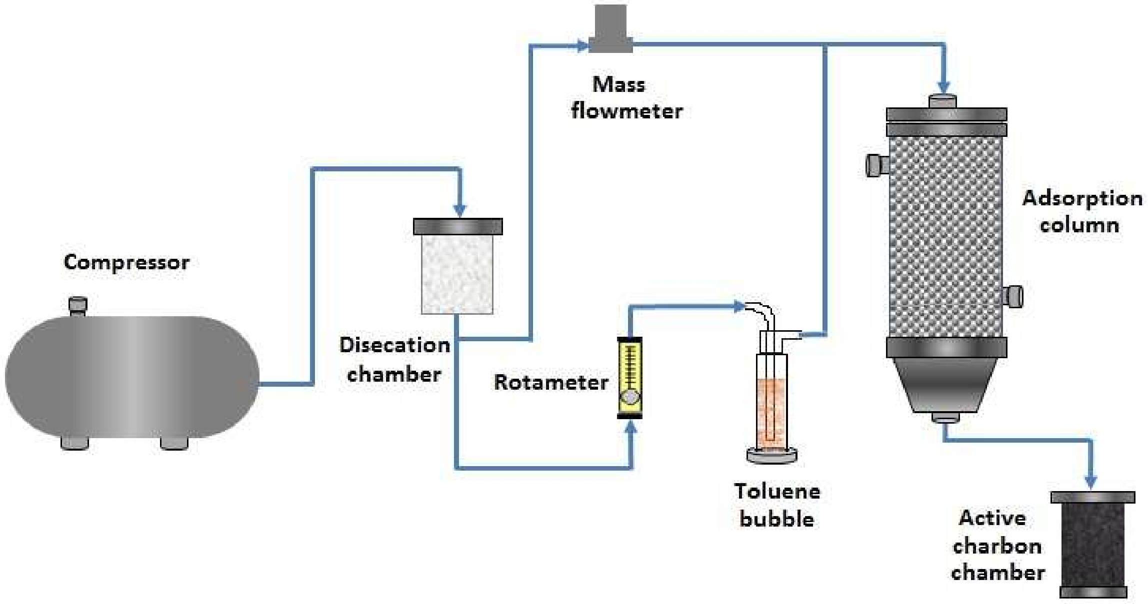


Figure 6.4 Experimental setup to determine toluene adsorption isotherm at 25°C with dry inlet air and dry packing material.

6.2.7. Soil conditioning, acclimation and inoculation process

Unlike industrial materials commonly used in biofilters, the supports proposed in this study are heterogeneous materials of varied particle size which need to be conditioned. Therefore, they were sieved in order to determine the particle size distribution. Furthermore, the material may include inert waste such as stones which should be removed before introducing it into the biofilter.

In order to acclimate soils, a contaminated stream was passing through it. It is expected that during the start-up of the system and the acclimation period, the soil’s indigenous biomass will specialize in removing the target contaminants in the study. If the soil does not have any indigenous biomass or it is necessary to minimize the acclimation period, the use of activated sludge from a wastewater treatment plant (WWTP) as external inoculum is proposed (Gallastegui *et al.*, 2013). This aqueous medium, derived from a biological process, usually contains diverse bacteria strains which are able to degrade several contaminants.

To carry out the inoculation, and in considering the volume of soil selected, an amount of 150 mL of inoculum was estimated in order to water the bed. This operation favoured the development of a biomass capable of degrading the contaminants in less than a month, which is the time spent in the acclimation step.

6.3. Results and discussion

Soil characterisation and results concerning biofilter operation are presented in this section. These results enable the identification of the key strengths and weaknesses of each soil to be used in biological processes. In general, an ideal packing material for biofiltration must exhibit high porosity (0.4-0.8) (Devinny *et al.* 1999), high specific surface area (300-1000 m^2 m^{-3}) for biomass attachment and contaminants adsorption (Dumont and Andres, 2010; Herrygers *et al.*, 2000), good structural strength, good moisture retention, good pH buffering capacity and a low bulk density. In the case of planted biofilters, the needs are different as plants have other requirements to growth than those demanded by microorganisms alone, such as total organic matter, humic and fulvic acids, cation exchange capacity, content of phosphore, potassium and, other elements.

6.3.1. Soil characterization

Two groups of parameters were established to determine the soil properties. The first group (Group I) characterises the organic nature of the support and the second one, the physic-chemical properties. Group I includes properties associated with the ions and their regulatory capacity (pH, neutralization potential, conductivity and cation exchange capacity), carbon source, humic and fulvic acids and nutrient content. Group II includes moisture content, surface area, pore size and particle size. Photographies of Soil-1 and Soil-2 are presented in Figure 6.5.


(a) (b)

Figure 6.5 Soil-1 (a) and Soil-2 (b).

6.3.1.1. Results Group I. Properties associated with the organic nature of the support

In order to analyse characterization results, parameters determined in soils were simplify to those of interest for biofiltration process. Table 6.5 shows the most relevant properties of both soils and their importance in biological treatments (biofiltration and botanical filtration).

These parameters must encourage and promote colonization and metabolic activity of the microorganisms acclimated to the media, generating the biodegradation of contaminants. All other properties related to the nature of the two soils, as well as the techniques used in their determination are presented in Annexe 6.A

According to the properties describing in Table 6.5, some parameters can be highlighted in order to compare both soils. The moisture content has a significant influence in biofilter efficiency. Even if Soil-1's moisture is 7.8 times higher than the moisture of Soil-2, both soils will need to be watered as many studies suggest that to achieve optimum and sustained biofilter performance in the treatment of hydrophobic VOCs, moisture content of packing material should be in the range between 30 % and 60 % (van Lith *et al.*, 1997; Nikiema *et al.*, 2007; Sun *et al.*, 2002). In the case of planted biofilters, the need of water will be determined by the plant species involved.

Table 6.5 Principal physic-chemical properties of Soil-1 and Soil-2.

Parameters	Value		Comments
	Soil-1	**Soil-2**	
Moisture content (%)	19.4	2.5	Critical parameter which influences plant/microbial growth and activity.
pH	9.0	7.0	Soil pH affects the soil's physical, chemical, and biological properties and processes.
Total organic matter (%w/w)	5.29	4.26	It serves as a reservoir of nutrients, provides soil aggregation, increases nutrient exchange, retains moisture, reduces compaction and increases water infiltration.
Total organic carbon (% w/w) = Total organic matter/1.72[a]	3.08	2.48	Organic carbon is the primary source of energy for soil microbes.
Total Nitrogen (% w/w)	0.18	0.04	Nitrogen is critical to sustain biomass growth.
Relation C/N	14.59	59.33	Traditional guide to the nature of the organic matter present in the soil.
Total humic extract (%w/w)	1.48	1.9	Humic substances interact with metal ions, oxides, hydroxides, mineral and organic compounds, including toxic pollutants, to form water-soluble and water-insoluble complexes.
Humic acids (%w/w)	1.24	1.24	Humic acids (HAs) function as important ion exchange and metal complexing (chelating) systems.
Fulvic acids (%w/w)	0.25	0.66	The exchange capacity of fulvic acids is more than double that of humic acids.
Cation-exchange capacity (CEC) (meq de Na/100g)	15.5	7.7	Property of a soil that describes its capacity to supply nutrient cations to the soil solution for plant uptake.

[a] Estimation suggested by Hoyle, 2015.

%w/w: dry soil weight basis

On the basis of organic matter content, soils are characterized as mineral or organic (United States Department of Agriculture, 1999). In this case, both soils are mineral as they contain less than 20-30% organic matter (see Table 6.5). The value of this parameter is low for both soils which let infer, at the beginning, that they are not a good material for planted biofilter and/or simple biofilters. Indeed, soils with medium to high levels (10-30%) of organic matter would generally be expected to have good structure, moisture retention and better nutrient exchange (Brady and Weil, 2002), features wanted in biofilter packing materials. Nevertheless, other properties such as the pH, the relation C/N and the organic carbon are also important in biological processes.

The pH is an important parameter that influences biological processes efficiency. Soil-1 has an optimum value because most of the BTEX depredated microorganisms in biofilters develop at a pH of 7 (Mudliar *et al.*, 2010). Conversely, Soil-1 has a pH value at which the degradation of TEX will be limited. Even so, the pH of the environment can be controlled by adjusting the pH of the nutrient solution.

Optimum values for C/N ratio depend on the nature of the organic matter (Brady and Weil, 2002). The basic premise behind this ratio is that organic carbon is the primary source of energy for soil microbes, but these also require nitrogen to multiply and utilize this energy (Miller, 2000). The high value of C/N ratio in Soil-2 is due to the low quantity of nitrogen. Nitrogen makes up the largest fraction of dry cell mass and is thus critical to sustain biomass growth and VOC degradation capacity (Song *et al.*, 2003). Accordingly, an external nitrogen source must be provided. Even though Soil-1 has a higher content of N, it could not be sufficient as a rapid decrease in nitrogen level will be take place in the first days of biofilter operation which was observed by Song *et al.* (2003) while treating toluene and p-xylene at loads of 20.3-47.3 g m^{-3} h^{-1} and 21 g m^{-3} h^{-1}, respectively, in a lab-scale biofilter.

Song *et al.* (2003) also stated that values higher than 0.03 mg N par mg of COD (chemical oxygen demand) are necessary to maintain high biofilter removal efficiency. Values of 0.01 and 0.003 mg N/mg COD were calculated for Soil-1 and Soil-2, respectively, using the relation COD=7.25+2.99TOC (Dubber and Gray, 2010) to have an idea of the COD value. Nitrogen deficiency is herein confirmed, hence the addition of nitrogen to the biofilters working with Soil-1 or Soil-2 will be necessary in order to avoid the operation under nitrogen-limited conditions.

Humic substances are the largest constituent of soil organic matter. They play an important role in soil fertility and thus, it is an important parameter in the case of planted biofilters. They have an important influence over the soil structure, porosity, water holding capacity, cation and anion exchange, and are involved in the chelation of mineral elements. Soil-1 and Soil-1 have similar values in these parameters (total humic extract, humic and fulvic acids). Considering the cation-exchange capacity (CEC), Soil-1 has a value twice higher than Soil-1 which means that Soil-1 will have greater water holding capacity (Ketterings *et al.*, 2007) and a higher ability to hold onto essential nutrients. As microorganisms need macronutrients and micronutrients to growth, their availability must be guaranteed either by the filtering material or by external nutrient-solution addition.

6.3.1.2. Results Group II.- Physic-chemical properties

Wettability

Results are shown in Figure 6.6. Wettabilities of Soil-1 and Soil-2 are low as they are only able to absorb about 18 and 10 g_{H2O} $kg^{-1}_{support}$, respectively, directly from the air stream saturated in water vapour. This value indicates the need to control exhaustively moisture content by carrying out irrigation when the humidity range is not adequate.

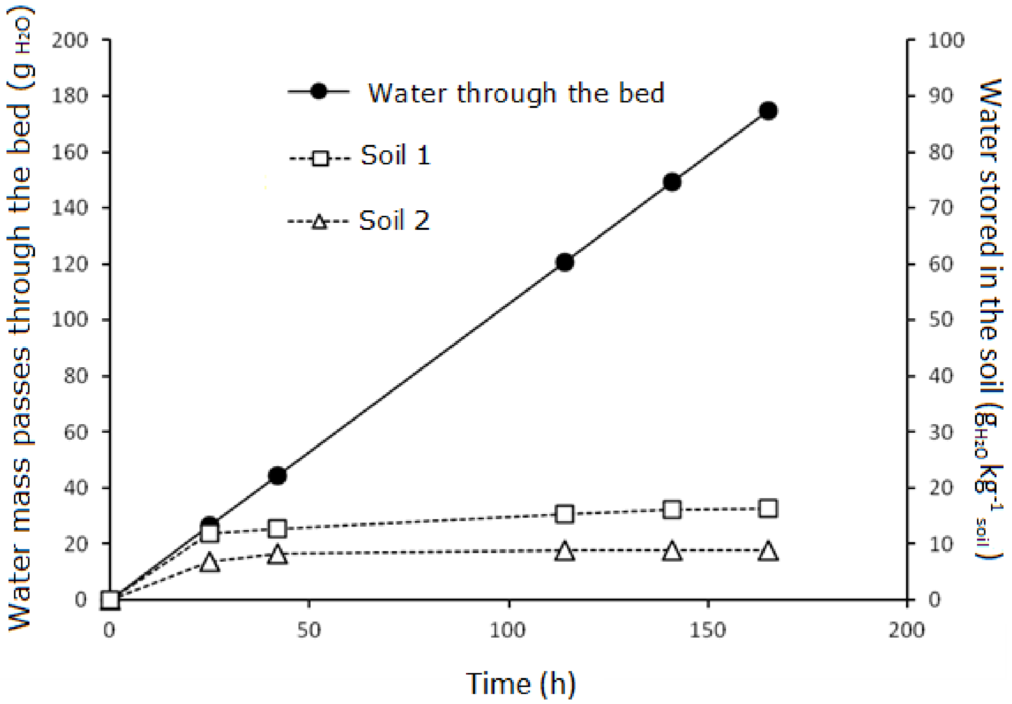


Figure 6.6 Evolution of the soils' moisture content during drying process.

Surface area and pore size

In Table 6.6 are presented the results obtained in this part of the characterization of Soil-1 and Soil-2. It was decided to separate Soil-2 differentiating between organic and inorganic fraction due to the heterogeneity of the elements forming the sample. This measure was correct based on the values of superficial area and average pore size for both parts of Soil-2 (organic and inorganic) which are slightly different.

Table 6.6 Superficial area, volume and average pore size for Soil-1 and Soil-2

Sample	Superficial	Pore volume	Average

	area ($m^2\ g^{-1}$)	($cm^3\ g^{-1}$)	pore size (Å)
Soil-1 (Total)	3.717	1.218×10^{-2}	64.10
Soil-1 (organic fraction)	1.897	5.021×10^{-3}	51.30
Soil-1 (inorganic fraction)	5.063	5.959×10^{-3}	26.70

Comparing with the most common natural and synthetic materials (see Table 6.7), soils under study show an intermediate specific surface area within certain organic substances (values between 0.5 and 18.4 $m^2\ g^{-1}$), and both soils show two orders of magnitude lower than inorganic materials with higher surface area (activated carbon > 900 $m^2\ g^{-1}$ and zeolite 500 $m^2\ g^{-1}$). However, the relatively high value of specific surface area is related to micro-pores whose size is less than 1 µm, indicating that the majority of pores are not accessible to the microorganisms (size 1-10 µm) because they will be saturated with irrigation water and condensation processes.

Typically, problems associated with a low porosity can be solved with larger biofilters (if physically possible), making the EBRT in the bioreactor more important.

Table 6.7 Superficial area for common materials used in biofiltration.

Sample	Superficial area ($m^2\ g^{-1}$)	Sample	Superficial area ($m^2\ g^{-1}$)
Activated carbon (1)	950.0	Lignite (1)	6.0
Granular activated carbon (3)	939.1	Bagasse (3)	4.5
Zeolite (4)	581.7	Compost (1)	2.8-3.7
Earthworm casting (4)	327.3	Coconut fibre (1)	1.7-6.9
Tire scrap (4)	87.6	Peat with heather (1)	1.4-1.5
Expanded Schists (2)	50.1	Coconut fibre (5)	0.9
Pine Barks (2)	18.4	Lava rock (1)	0.6
Crab shell (4)	18.1	Pine leaves (1)	0.5
Turba (5)	13.4	PUF (1)	0.02

[1] Dorado *et al.* (2010a); [2] Anet *et al.* (2013); [3] Mathur *et al.* (2007); [4] Kwon and Yeom (2009); [5] Pérez *et al.* (2015)

Particle size distribution

Average particle size and particle size distribution are among the most important characteristics when selecting a support. Particles that form the substrate must be large enough so that pressure drop is small and biofilm formation does not obstruct the passage of contaminated gas. Small particles could be dragged and accumulate in the larger pores or in the drainage system, blocking the biofilter working. Conversely, if the particles are too large, they cannot provide sufficient contact area between the gas stream and the active biofilm.

In general, a particle size greater than 4 mm in diameter is recommended (Swanson and Loehr, 1997). Figure 6.7 presents particle size distribution of Soil-1 and Soil-2. There is a higher percentage of particles larger than 2 mm in the case of Soil-1 (60 %) which could classified this soil in the gravel type according to the United States Department of Agriculture (1987). Soil-1, in contrast, has a percentage of 76 % of its particles below 2mm of diameter and, could be considered as sand type. Accordingly, Soil-1 (sand) will have the highest water holding capacity in front of Soil-2 which has a high presence of stones with lava rock aspect. Big spaces between these particles limit the water holding capacity but allow air into de soil (small pressure drop).

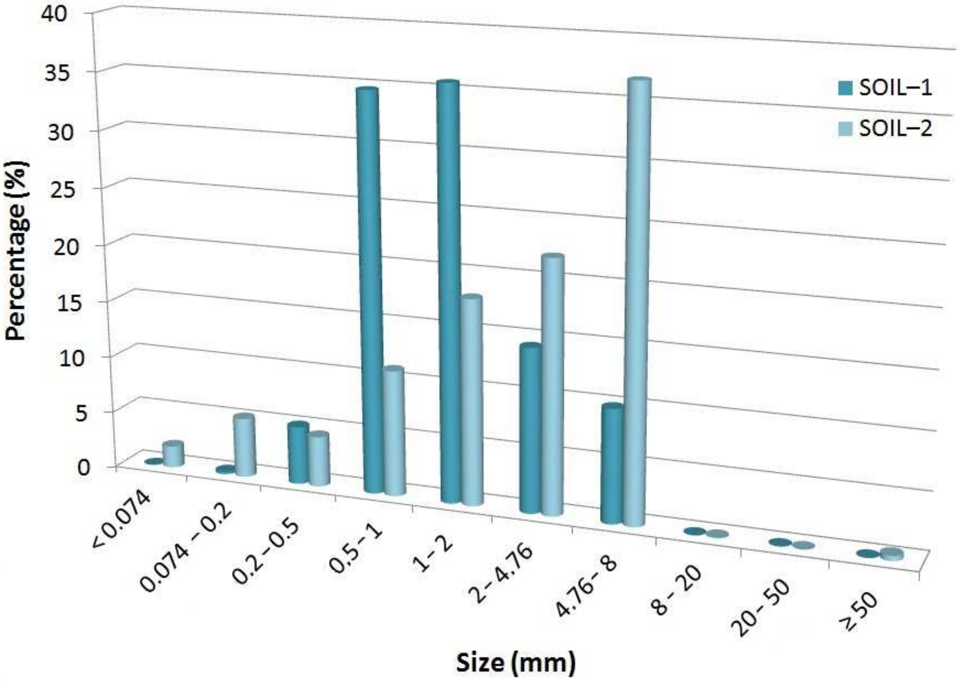


Figure 6.7 Particle size distribution for Soil-1 and Soil-2;

Other authors have reported the size distributions for other materials. For example, compost's particle size distribution was studied by Viswanathan *et al.* (2013). These authors found that 71 % of particles were smaller than 2 mm. Moreover, Yang *et al.* (2011) reported a percentage of more than 95 % for the same material in the same range. Other classic materials such as topsoil and peat are noted for their high percentage of particles in the rage of less than 0.8 mm (67 % and 91 %, respectively) (Yang *et al.* (2011)). In order to reduce this support deficiency, other materials with superior particle size distribution are often used together with the media such as wood bark (Wani *et al.*, 2000).

6.3.2. Results concerning pressure drop trials.

According to Figures 6.8 and 6.9, in dry conditions, pressure drop was low for both materials (between 1 and 7 mm H_2O $m^{-1}{}_{\text{biofilter bed}}$). As it can be seen on Figure 6.8, pressure drop values for Soil-2 showed a disorganised behaviour during the first 40 days (down-flow mode operation) whereas in Soil-1 the pressure drop increased with time. Nevertheless, at the end of this period both soils, Soil-1 and Soil-2, presented a pressure drop of 6 and 7 mm H_2O $m^{-1}{}_{\text{biofilter bed}}$, respectively. Concerning up-flow mode operation (Figure 6.9), the pressure drop was more stable and lower in Soil-2 than in Soil-1 which is consistent with the presence of stones in Soil-2 that favour the loose airflow through the bed.

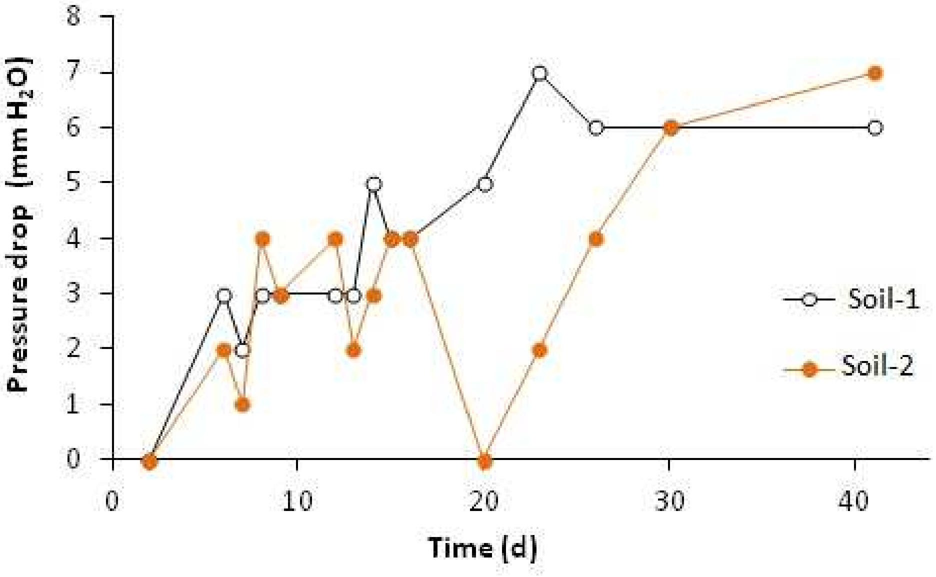


Figure 6.8 Evolution of the pressure drop during down-flow mode operation and dryness period.

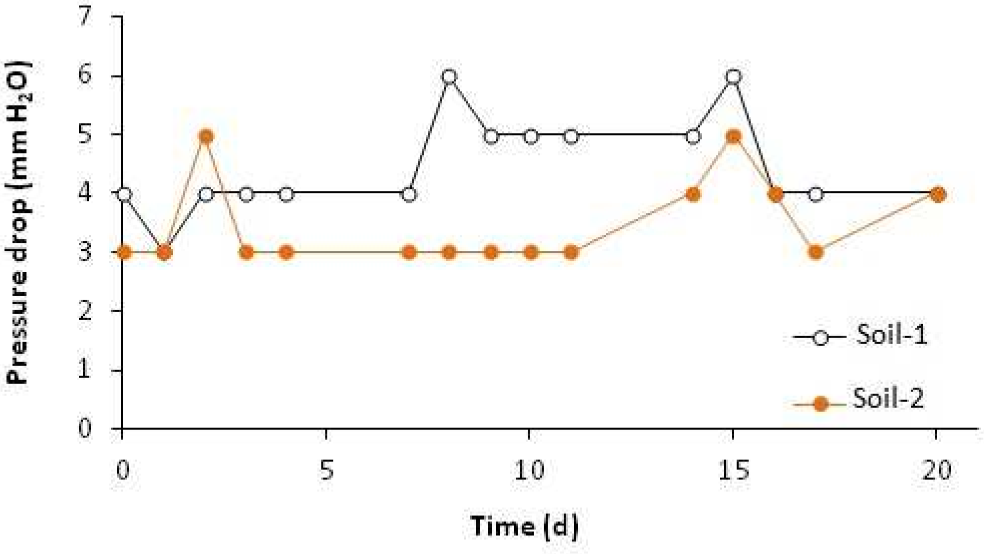


Figure 6.9 Evolution of the pressure drop during up-flow mode operation and dryness period.

Regarding the pressure drop during flooding trials, three consecutive tests were carried out as shown in Figure 6.10. Pressure drop reported its maximum value immediately after the addition of water which is consistent with what is reported in the literature (Dorado *et al.*, 2010). Afterward, pressure drop decreased with time. This reduction in the pressure drop could be explained by the fact that water content go down gradually and because preferential paths could be developed and consequently, the resistance to the air flow through the bed might be diminished.

The highest values of pressure drop were 30 and 8 mm H_2O $m^{-1}{}_{biofilter}$ for Soil-1 and Soil-2, respectively. Soil-2 shows better behavior in front of the flooding events which is probably due to the presence of stones similar to “lava rock”. Even if these values are not high, flooding conditions could induce higher values and therefore, limit the use of this kind of materials because, pressure drops cannot be superior to 153 mm H_2O m^{-1} (1500 Pa m^{-1}) from an economical viewpoint (Estrada *et al.*, 2012).

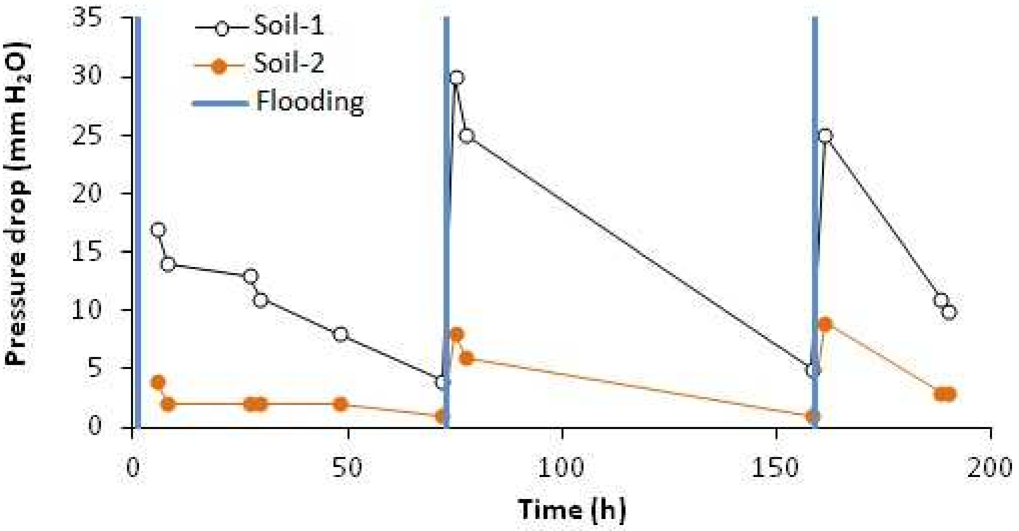


Figure 6.10 Evolution of the pressure drop in flooding conditions and upflow mode operation.

6.3.3. Results concerning adsorption tests

Results in the present study showed low adsorption capacity for both dried soils: between 0.28 and 2.20 mg $g^{-1}{}_{material}$ for Soil-1 and in the range of 0.20-1.28 mg $g^{-1}{}_{material}$ for Soil-2, considering the concentrations herein studied (<120 ppm). The adsorption of toluene onto different materials have been also studied by numerous authors for dry and wet different materials (Barona *et al.*, 2007; Maestre *et al.*, 2007; Bhaskaran *et al.*, 2007; Ortiz *et al.*, 2003; Delhoménie *et al.*, 2003; Dorado *et al.*, 2010; Alvarez-Hornos *et al.*, 2011). Their findings revealed that adsorption capacity of most of the tested materials was reduced between 40 to 90 % when the tests were carried out in wet materials. Accordingly, in real conditions (moisture content and humid inlet air), the adsorption capacity of Soil-1 and Soil-2 will be reduced and it can be negligible inside the biofilter in from of biological removal process.

6.3.4. Biofilter operation

Two biofilters, BF1 and BF2, were installed containing Soil-1 and Soil-2, respectively. Gas stream to be purified is introduced at the bottom of bioreactors (up-flow mode). Each biofilter bed is 8 cm high, for a total fill volume of 1.45 litres. Efforts were made to supply the same concentration of pollutants in two biofilters, although the biofilter containing Soil-2 worked at higher loads during some phases of the experiments. The biofilters were operated during 160 days and continuous and intermittent periods were established over this time as shown in Table 6.8.

Table 6.8 Operating conditions during continuous and intermittent periods in BF1 and BF2.

Parameter	**Acclimation**		**Continuous operation**		**8h ON/ 16h OFF**		**24h ON/ 24h OFF**		**Continuous operation**
Time (days)	1-30		31-130		131-140		141-155		156-160
EBRT (s)	150-180		80-90		80		80		80
BF1									
Concentrations	($g\ m^{-3}$)	(ppm)	($g\ m^{-3}$)	(ppm)	($g\ m^{-3}$)	(ppm)	(ppm)	($g\ m^{-3}$)	($g\ m^{-3}$)
Toluene	0.16	41	0.10	26	0.20	47	40-112	0.14-0.42	≈0.75
Ethylbenzene	0.16	35	0.15	35	0.14	33	15-107	0.06-0.47	
p-Xylene	0.05	12	0.04	8	0.04	14	12-28	0.05-0.12	
BF2									
Concentrations	($g\ m^{-3}$)	(ppm)	($g\ m^{-3}$)	(ppm)	($g\ m^{-3}$)	(ppm)	(ppm)	($g\ m^{-3}$)	($g\ m^{-3}$)
Toluene	0.10	27	0.10	26	0.10	29	36-152	0.14-0.57	≈1.10
Ethylbenzene	0.10	24	0.15	34	0.12	27	24-59	0.10-0.26	
p-Xylene	0.09	20	0.06	14	0.04	14	11-81	0.05-0.35	

6.3.4.1. Acclimation period (days 1-30)

The first month of operation is dedicated to acclimation, with an EBRT in the range of 150-180 s. In both biofilters, p-xylene concentrations were less than toluene concentration at the biofilters' inlet because of its recalcitrance characteristic and inhibitor behaviour reported in a previous study (Gallastegui *et al.*, 2011).

<u>Results concerning biofilter BF1 (Soil-1)</u>

In this first phase, biofilter was fed in average with 41 ppm (3.21 $g\ m^{-3}\ h^{-1}$), 35 ppm (3.10 $g\ m^{-3}\ h^{-1}$) and, 12 ppm (1.05 $g\ m^{-3}\ h^{-1}$) of toluene, ethylbenzene and p-xylene, respectively, and average removal efficiencies (RE) were 72, 64 and 53 % (Figures 6.11-6.14). Although a RE of 100 % was not reached in this first month, the inoculum was well adapted to the operational conditions (high EBRTs, saturation of inlet airstream) and did not reduce its ability to eliminate these contaminants.

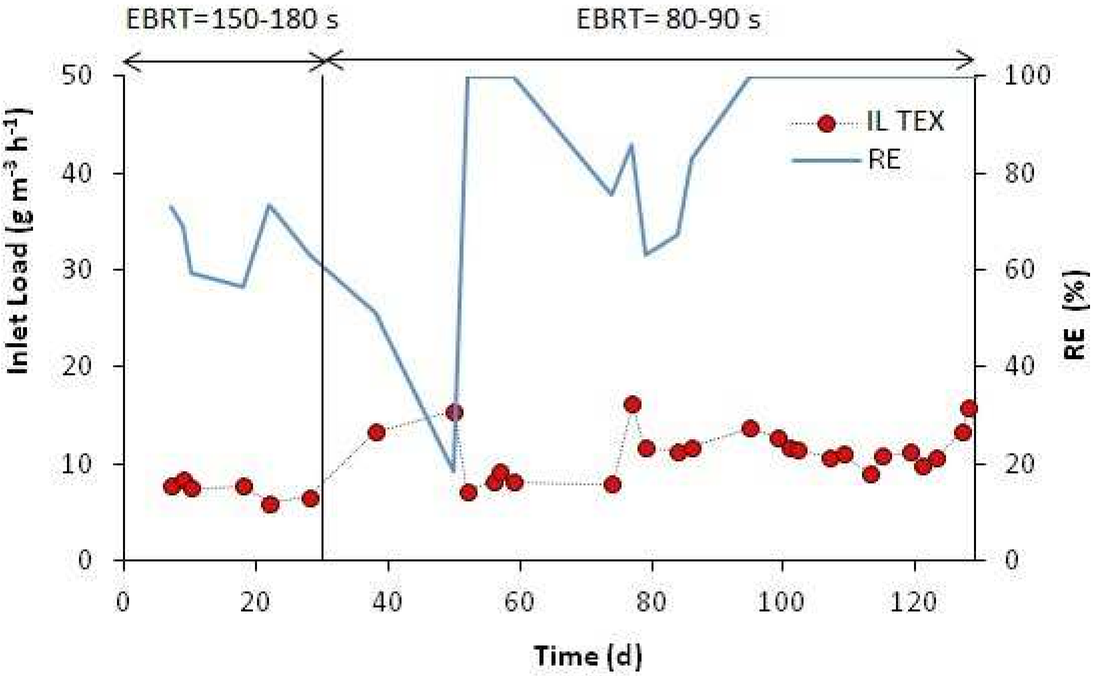


Figure 6.11 Evolution of the TEX inlet load and removal efficiency for BF1 (Soil-1)

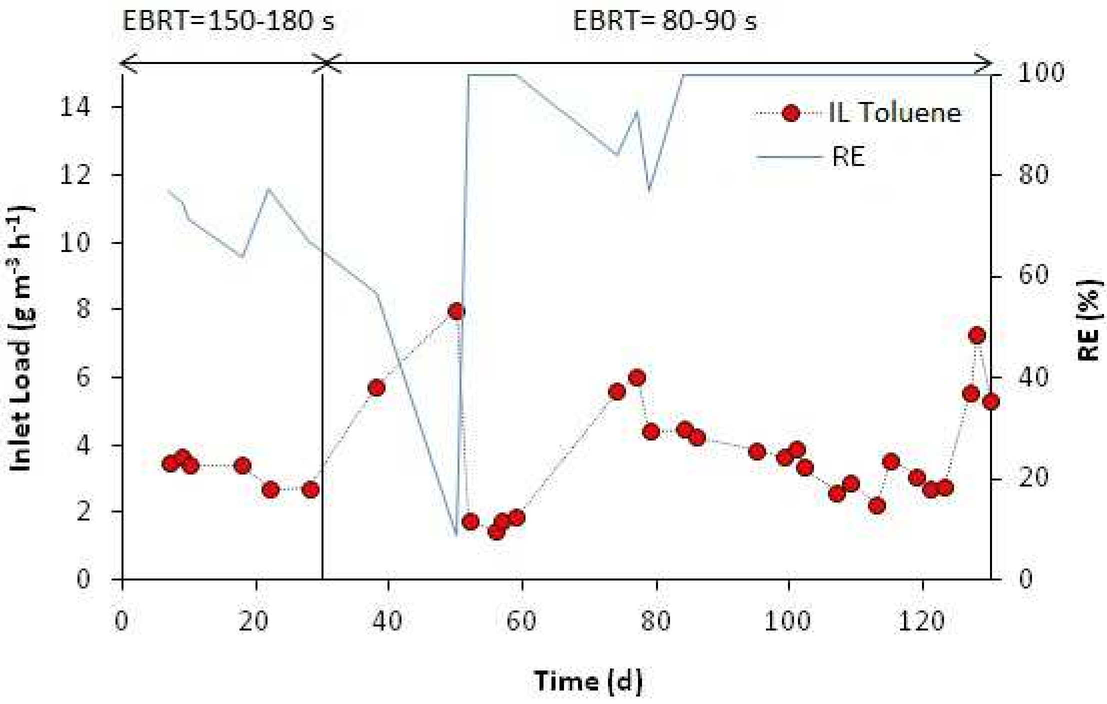


Figure 6.12 Evolution of the Toluene inlet load and removal efficiency for BF1 (Soil-1)

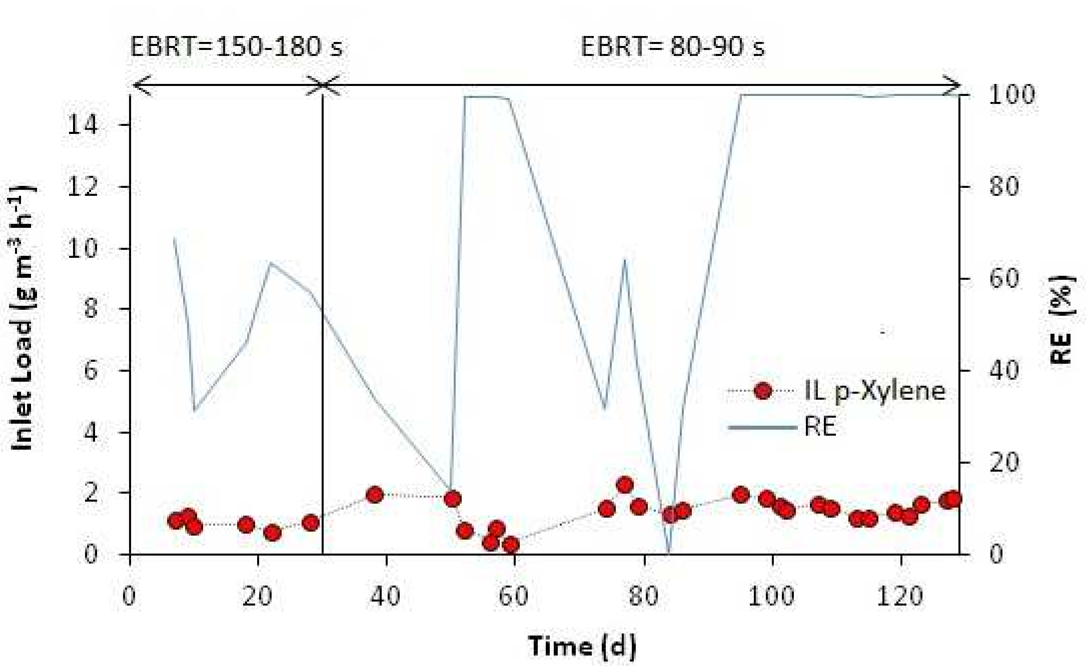


Figure 6.13 Evolution of the p-xylene inlet load and removal efficiency for BF1 (Soil-1)

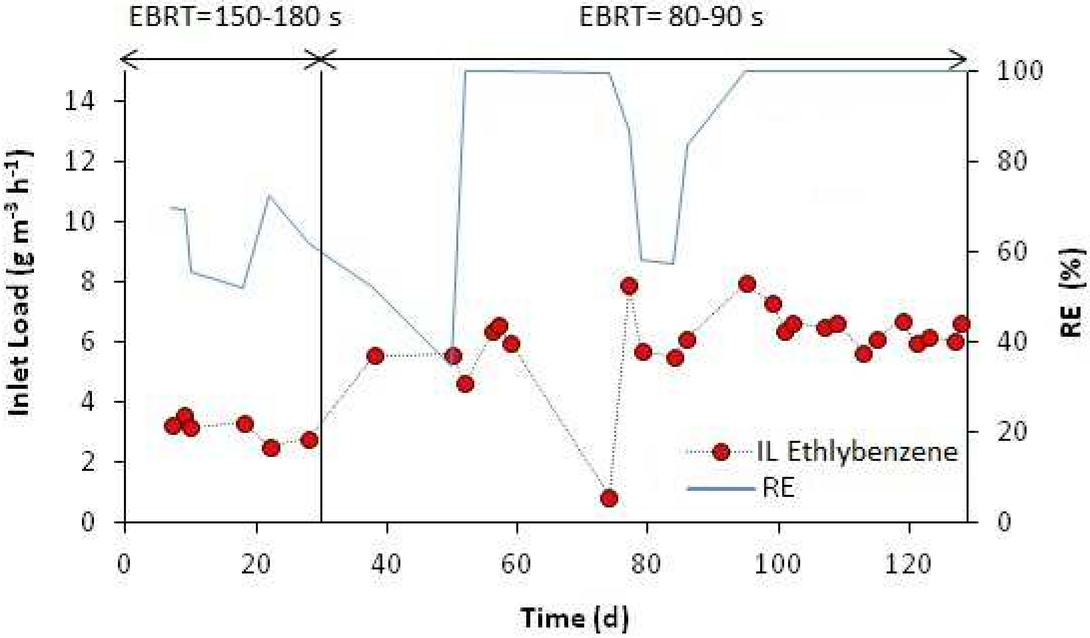


Figure 6.14 Evolution of the ethylbenzene inlet load and removal efficiency for BF1 (Soil-1)

Results concerning biofilter BF2 (Soil-2)

This biofilter was fed with 27 ppm (2.00 g m^{-3} h^{-1}), 24 ppm (2.01 g m^{-3} h^{-1}) and 20 ppm (1.72 g m^{-3} h^{-1}), in average, of toluene, ethylbenzene and p-xylene respectively, and average REs were 49, 46 and 30 %, respectively. The inoculum did not show signs of progressive growth in this case (Figures 6.15-6.18) compared to BF1. Despite not reaching optimal performance, EBRT was reduced as in the biofilter BF1 in order to compare the performance of both soils.

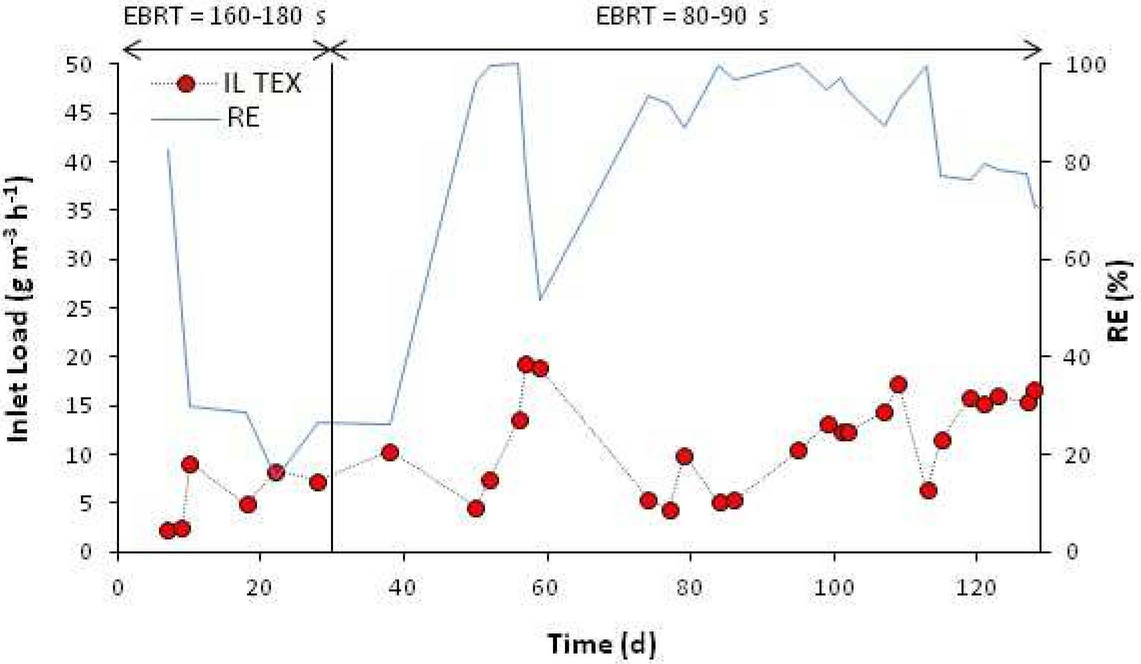


Figure 6.15 Evolution of the TEX inlet load and removal efficiency for BF2 (Soil-2)

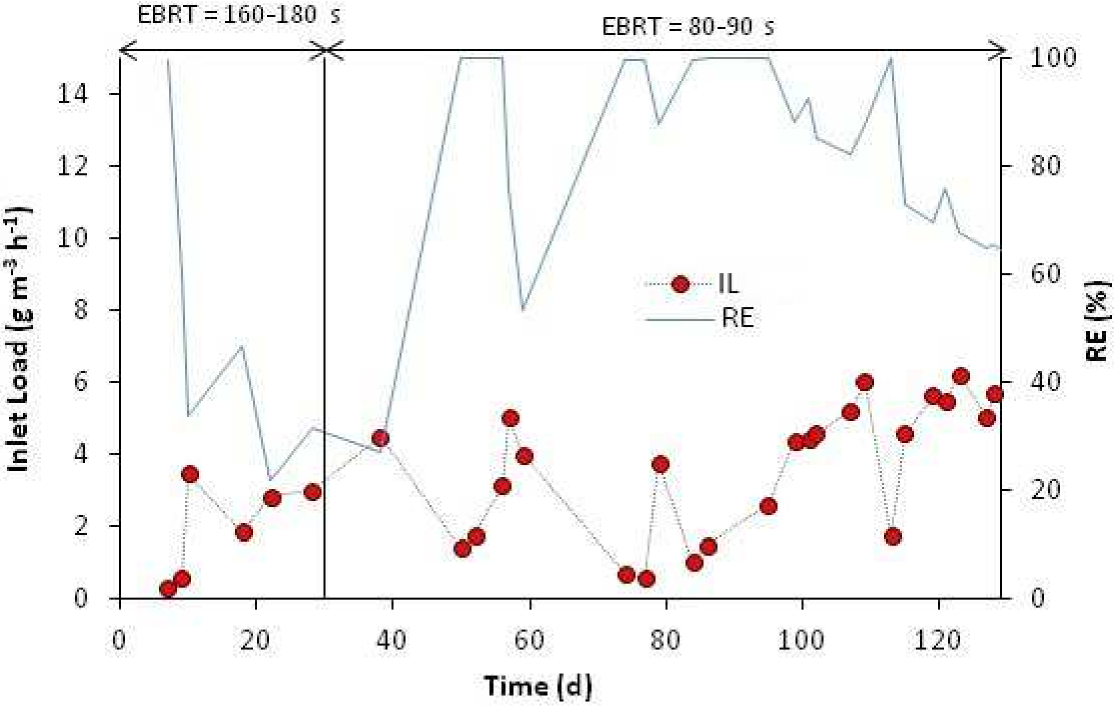


Figure 6.16 Evolution of the Toluene inlet load and removal efficiency for BF2 (Soil-2)

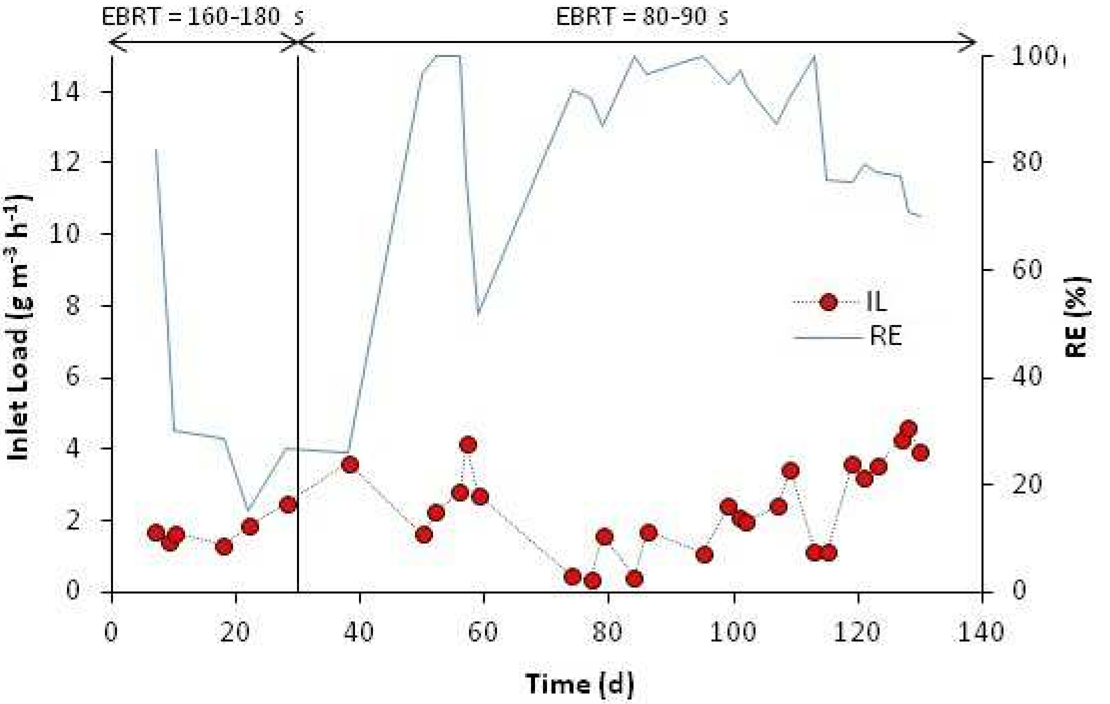


Figure 6.17 Evolution of the p-Xylene inlet load and removal efficiency for BF2 (Soil-2)

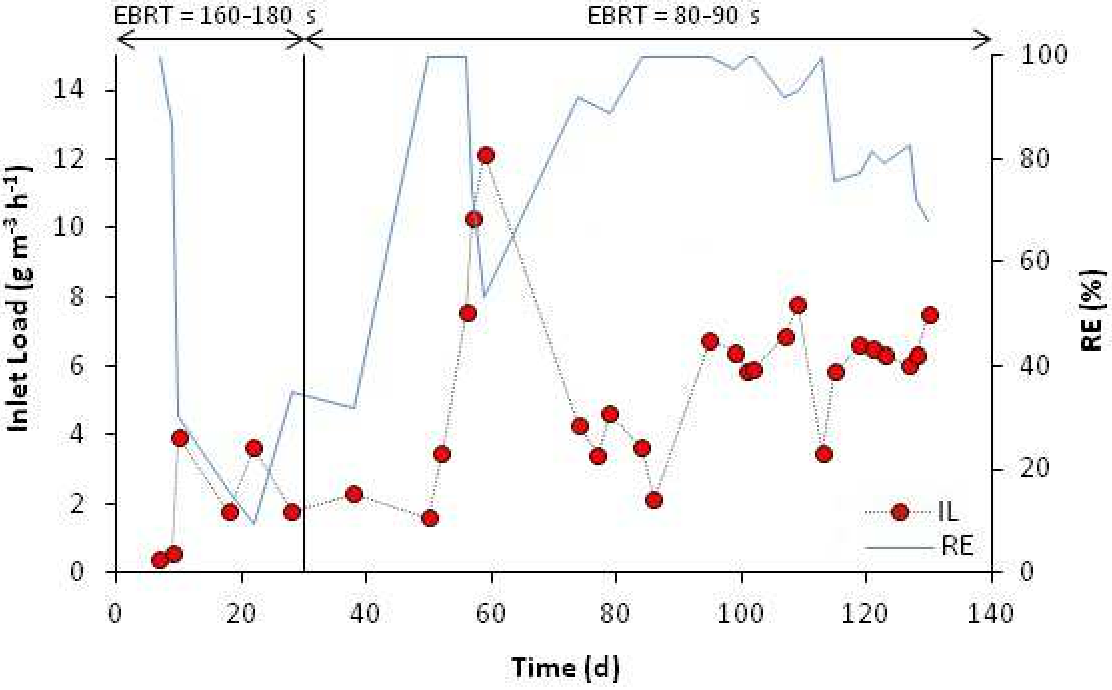


Figure 6.18 Evolution of Ethylbenzene inlet load and removal efficiency for BF2 (Soil-2)

Acclimation periods may vary from a few minutes to months (Table 6.9), depending on microbial community undergo acclimatization cell by biochemical changes, resulting in the development of the microorganisms ability to take advantage of the contaminant as the carbon source. Then the microorganisms responsible for the degradation of pollutants should be abundant enough to eliminate substances with high removal rates. Finally, these microbial communities must colonize all the support.

Table 6.9 Acclimation periods reported by other authors

Material	**Contaminant**	**Concentration ($g\ m^{-3}$)**	**Accclimation time (d)**	**EBRT (s)**	**Ref.**
Mixture of mature pig compost and polyethylene	NMHC, toluene, benzene	0–16	35	266	(1)
Mixture of compost, sugar cane bagasse and granulated activated carbon	BTEX	0.42	30	138	(2)
Compost/wood chips mixture	Propylene and butylene	1.6 – 119.5 0.2–2.5	84–91	390–960	(3)

^{1} Wu *et al.* (2009); ^{2} Mathur *et al.* (2007); ^{3} Rani *et al.* (2011)

In the case of TEX (toluene, ethylbenzene and xylene), there are examples of the use of inoculums both adapted and non adapted as a previous step to introduction into the biofilter. Alvarez-Hornos *et al.* (2008) used an inoculum obtained after acclimating to ethylbenzene for 2 months, a culture obtained from activated sludge secondary clarifier in a WWTP. This allowed 100 % removal efficiency from the first day.

Hwang *et al.* (2007) used a pre-acclimated inoculum to p-xylene from activated sludge to start a biofilter. For a concentration of 50 ppmv, the efficiency was 40-50 % during the first days (2-5) and then established about 85-90 % during days 10-25. Nevertheless, being bioreactors not operating under sterile conditions with changes in pollutant and its concentrations, the introduction of foreign microorganism strains to the system with specific environmental conditions makes its presence limited and disappear with time. For example, Perez *et al.* (2015) observed by characterization DGGE (Denaturing Gradient Gel Electrophoresis) that strains of "P. putida CECT 324" inoculated to two biofilters equipped with peat and coconut fibers for the treatment of styrene disappeared after 105 days of operation.

Quinlan *et al.*, (1999) used pre-acclimated inoculums to the presence of BTEX (times not specified). Optimum removal efficiencies were achieved from the fifth day in a biofilter equipped with a bed of composted forest products, sludge, lime and perlite.

6.3.4.2. Continuous operation (days 31–130)

From day 31, the EBRT was reduced to 80-90 s. This residence time may be considered a demanding value to evaluate the performance of bioreactors and can be compared to those installed at industrial scale.

Results concerning biofilter BF1 (Soil-1)

During the continuous operation (days 31 to 130), biofilter is fed with an average of 26 ppm (4.16 g m^{-3} h^{-1}), 35 ppm (6.44 g m^{-3} h^{-1}) and 8 ppm (1.47 g m^{-3} h^{-1}) of toluene, ethylbenzene, p-xylene, respectively.

The biofilter reached a stable RE of 100% from day 95 of operation (Figure 6.11). As seen in Figures 6.12 to 6.14, toluene was the first to reach the maximum degradation (day 84), while both ethylbenzene and p-xylene was completely degraded from day 95. It has to be noted that the RE was highly influenced by changes in the inlet load.

From day 95 to 130, the biofilter did not suffer any alteration, and removal efficiency was 100% at all times thanks to the appropriated control of operating conditions.

Figure 6.19 shows that biofilter BF1 did not reach its maximum degradation capacity, which means that it is able to treat higher concentrations of contaminants than those fed in this study (an average load input of 12 g m^{-3} h^{-1}). The results for every compound are shown in Figures 6.B1-6.B3 in Appendix B.

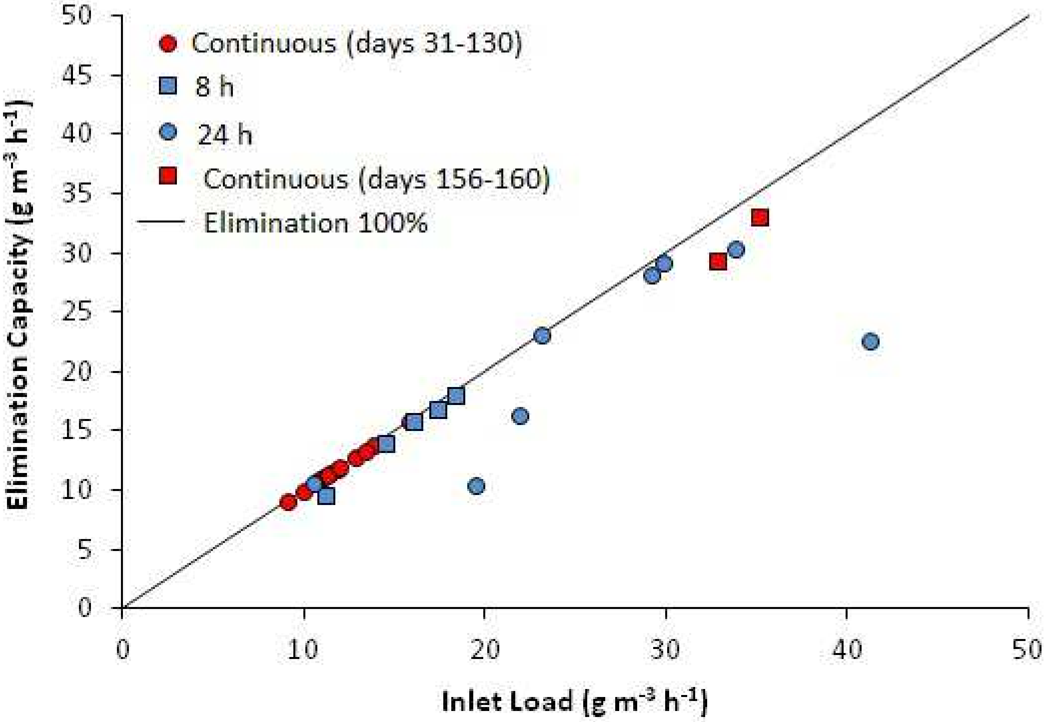


Figure 6.19 Inlet load vs. elimination capacity for TEX in BF1.

Results concerning biofilter BF2 (Soil-2)

During the continuous operation, an average of 26 ppm (4.16 g m^{-3} h^{-1}), 34 ppm (6.23 g m^{-3} h^{-1}) and 14 ppm (2.58 g m^{-3} h^{-1}) of toluene, ethylbenzene, p-xylene, is supplied to the biofilter respectively. The biofilter only reached 100 % of RE at specific times (days 84, 95 and 113) (Figure 6.15). Simultaneously, it can be seen that maintaining relative high concentrations for a long period of time (days 119-130) makes the performance of the biofilter worse gradually.

In this case (unlike the BF1, Soil-1), it is observed that the biofilter has reached its maximum elimination capacity for that EBRT; its value is around 13 g m^{-3} h^{-1} (Figure 6.20). Analyzing each pollutant, the maximum capacity of BF2 to remove toluene is 4.5 g m^{-3} h^{-1}, p-xylene from 3.0 to 3.5 g m^{-3} h^{-1} and ethylbenzene 6.5 g m^{-3} h^{-1} (Figures 6.B4-6.B6, Appendix B).

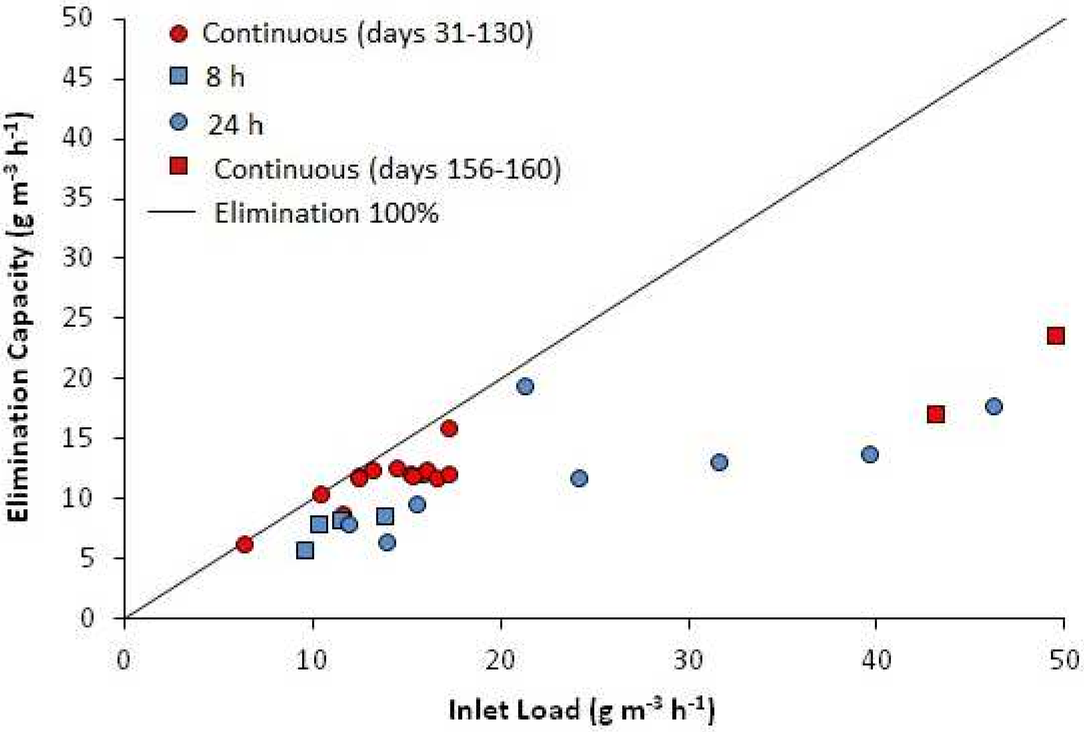


Figure 6.20 Inlet load vs. elimination capacity for TEX with Soil-2.

Nevertheless, it is necessary to keep in mind that if a biofilter is designed to eliminate concentrations as for example 100 ppm, its performance when subjected to high contaminant concentrations regularly cannot be a decisive factor in evaluating its capacity. Thus, Li *et al.* (2014) already warned that in many biofiltration studies, bioreactors were subjected to loads of pollutant concentrations much higher than those actually found in actual cases.

On the other hand, it should be ensured that the concentration of pollutants at the entrance of the biofilter is high enough to guarantee microbial growth. As reported in the literature, typical concentrations of trace gases (1-10 mg m^{-3}) could not ensure that growth (Guieysse *et al.*, 2008). Nevertheless, as demonstrated in a previous chapter (Chapter 4) and by Ondarts *et al.* (2012), even at low pollutant concentrations (µg m^{-3}) biofiltration is possible.

6.3.4.3. Biofilter performance during intermittent periods

Severe working conditions have been implemented for testing biofilter performance:

a) 8h ON / 16h OFF: During 10 days, contaminated gas passed through the biofilter 8 hours per day and the other 16 hours only humid air was introduce to the system.
b) 24h ON / 24 OFF: In a second period of 15 days, a regime of operation during which contaminated gas stream was fed to the system every other day, so that air did not pass during weekends or one in two days. Contaminant concentrations were doubled during this test.
c) Finally, continuous operation was re-established to test the resilience of the microbial community and see if it is able to recover the removal efficiency reached before this period.

Changes of operating conditions are presented by vertical lines in figures presenting these results.

<u>Regime of 8h ON/16h OFF (days 131–140)</u>

- *Results concerning biofilter BF1 (Soil-1)*

In this period of 10 days, the biofilter was fed with an average of 47, 33 and 14 ppm of toluene, p-xylene and ethylbenzene respectively. RE was slightly affected when its operation pass from continuous to 8h per day (for the 3 pollutants). Changes were mainly due to the stop during the weekends (65h OFF), especially after the second weekend (day 140) as shown in Figure 6.21.

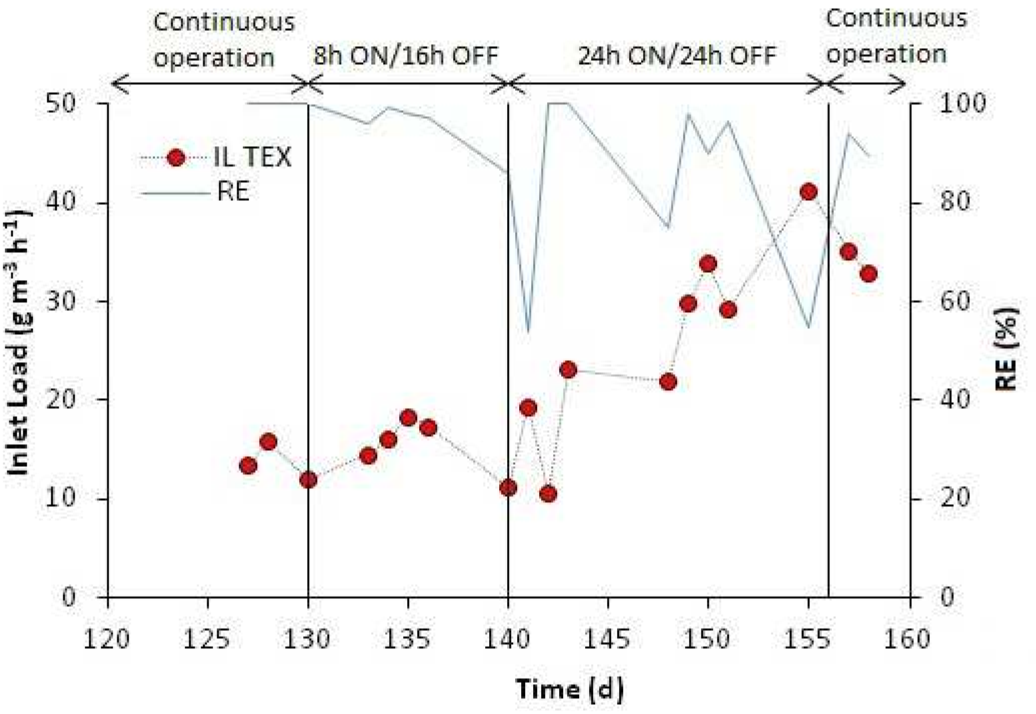


Figure 6.21 Evolution of TEX inlet load and elimination capacity for BF1 during intermittent periods.

In this case, the overall removal efficiency dropped by 14 % compared to 4 % after the first weekend (day 133), and in both cases the p-xylene is the compound that takes longer to recover from the intermittent regime (resilience after disturbance: p-xylene<toluene <ethylbenzene) (Figures 6.23-6.25 showed here below).

- *Results concerning biofilter BF2 (Soil-2)*

Average concentrations of 29, 27 and 14 ppm of toluene, p-xylene and ethylbenzene respectively were supplied to BF2. In Figure 6.22 it appears that discontinuous operation clearly affected the performance: in continuous operation, the maximum removal capacity was around 13 g m^{-3} h^{-1}, whereas in this case the maximum removal capacity was reduced to 9.8 g m^{-3} h^{-1}. Besides, the biofilter seems equally affected both on weekdays and weekends.

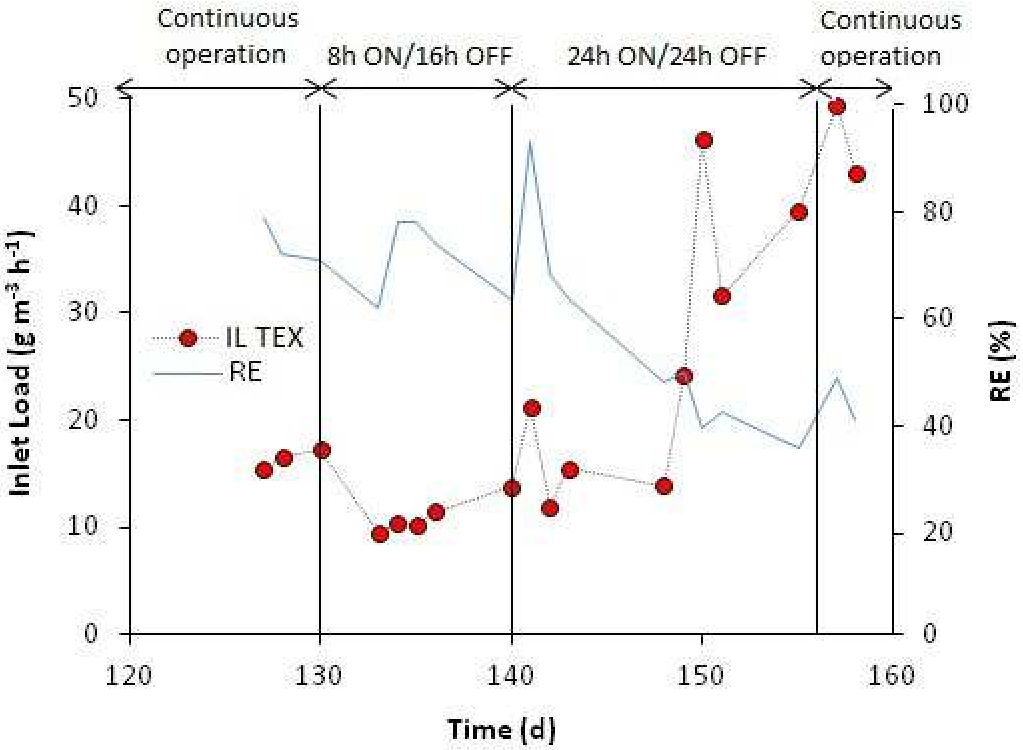


Figure 6.22 Evolution of TEX inlet load and elimination capacity for BF2 during intermittent periods.

Regime alternate days (24h ON/24h OFF) (days 141–155)

- *Results concerning biofilter BF1 (Soil-1)*

During this period, increasing concentrations of contaminant were supplied to the biofilters starting in a load of 19.4 g m^{-3} h^{-1} and concluded with 41.2 g m^{-3} h^{-1}. Thus, the aim was to observe the resilience of the support after stopping 24h and progressive increases in pollutant loading. Contaminant concentration ranges were as follows: toluene (40-112 ppm), ethylbenzene (15-107 ppm) and p-xylene (12-28 ppm).

As in the case for "8h ON / 16h OFF" biofilter performance is different weekdays and weekend. There are 3 spots to highlight (Figures 6.23 - 6.25):

- In day 141, after the change of "8h ON / 16h OFF" to "24h ON / 24h OFF", the performance drops from 100 % to 54 %.
- In days 148 and 155, both after weekends, the elimination capacity decreases about 25 % of the theoretical value compared with data collected during weekdays. Therefore, it is observed that the biofilter performance is degraded when subjected to longer than 2 days stops. This decrease in performance does not seem to be affected by changes in the contaminant's concentration (from 0.24 to 0.93 g m^{-3}).
- p-Xylene degradation ability was again the most affected (after the 2nd weekend, day 155, the removal efficiency was zero), the ethylbenzene suffered less during intermittent regime. Toluene removal efficiency recovered last days.

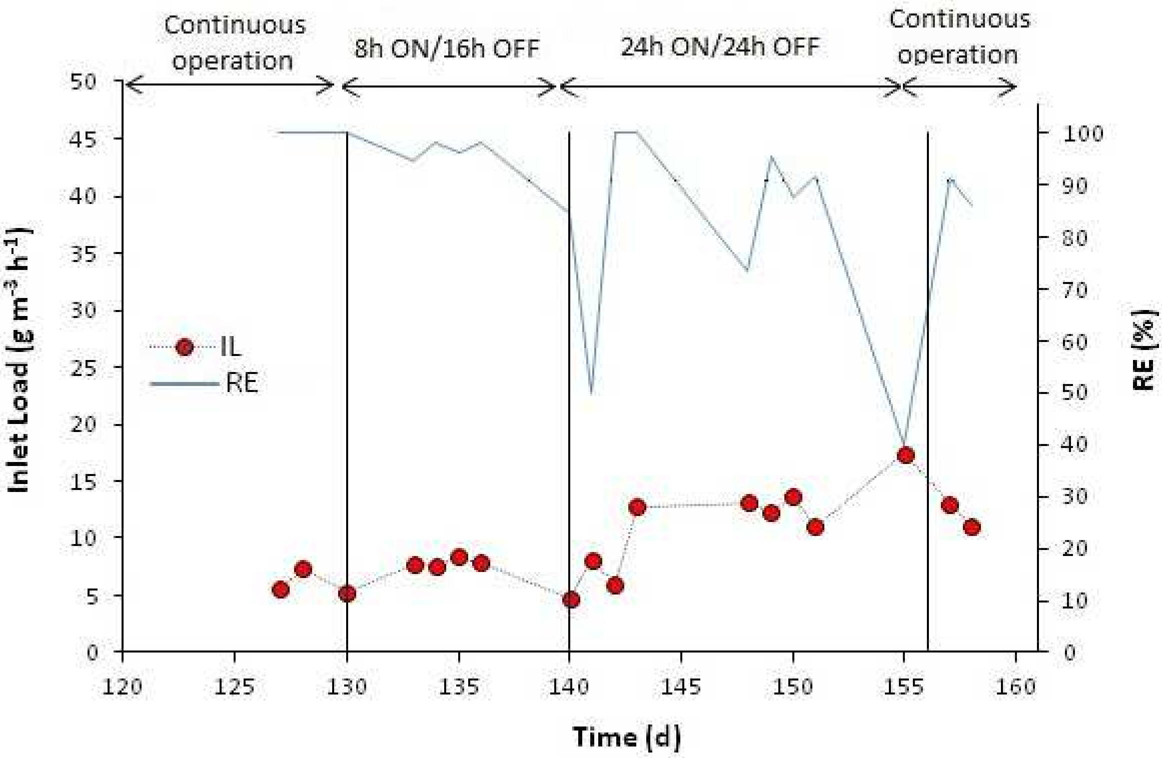


Figure 6.23 Evolution of Toluene inlet load and elimination capacity for BF1 during the intermittent period.

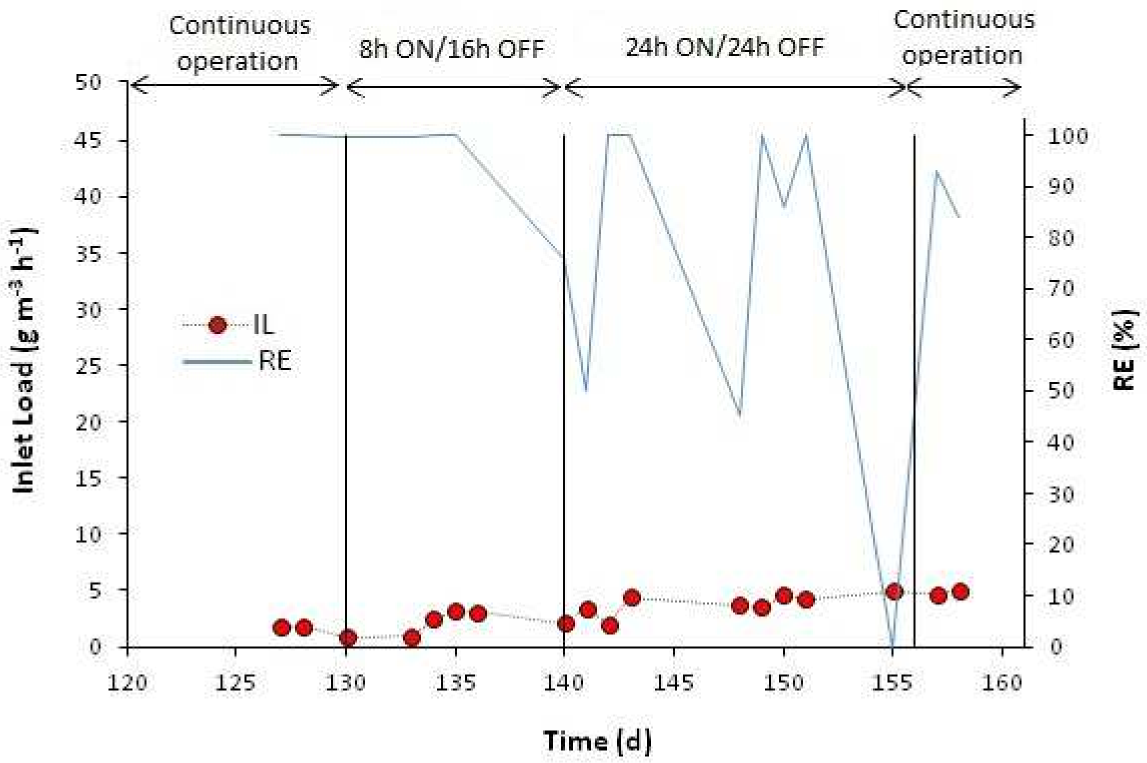


Figure 6.24 Evolution of p-Xylene inlet load and elimination capacity for BF1 during the intermittent period.

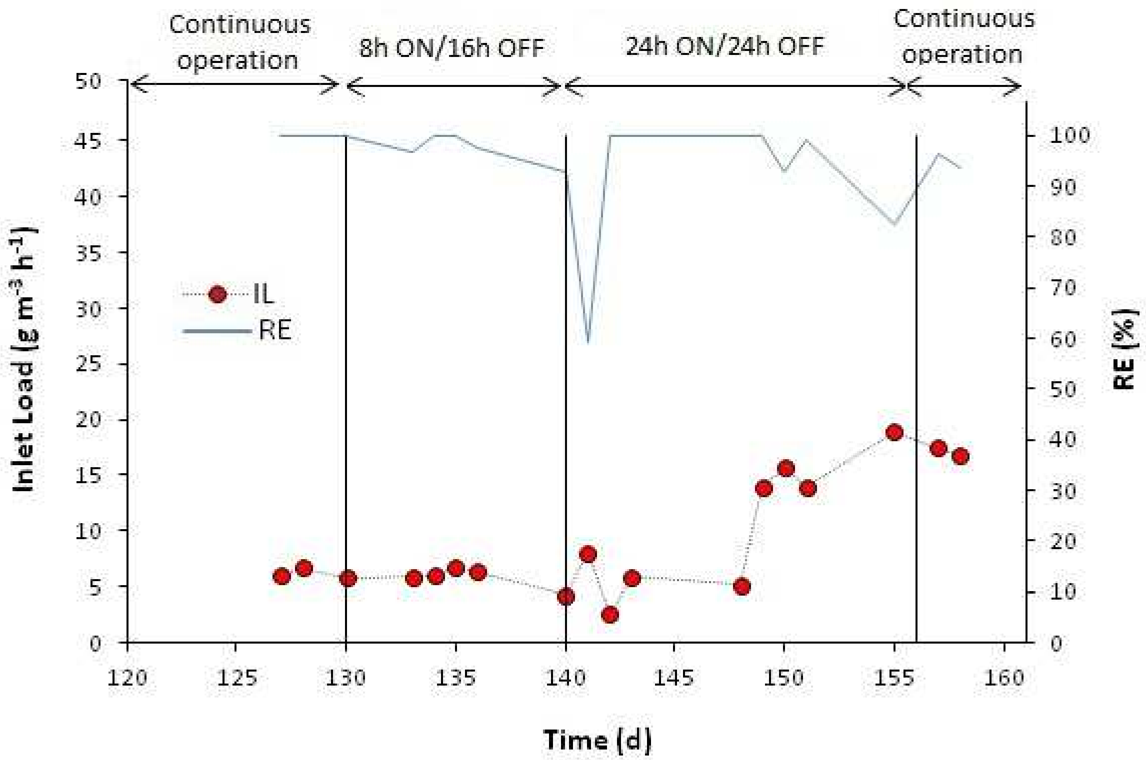


Figure 6.25 Evolution of ethylbenzene inlet load and elimination capacity for BF1 during the intermittent period.

- *Results concerning biofilter BF2 (Soil-2)*

Contaminant concentrations from 21.2 g m^{-3} h^{-1} to 49.5 g $m^{-3}h^{-1}$ were supplied to BF2. Biofilter resilience was studied under progressive increases in pollutant loading and operational alternate periods (24h ON/24h OFF). Contaminant concentrations were as follows: toluene (36-152 ppm), ethylbenzene (24-59 ppm) and p-xylene (11-81 ppm).

Global elimination capacity of Soil-2 decreased until 35 % in day 155 for a TEX pollutant load of 40 $gm^{-3}h^{-1}$. As in the case for "8h ON / OFF 16h", performance didn't change between weekdays and weekend (Figure 6.22). This is a poor elimination compared to 77 % in regime "8h ON / 16 OFF" and to 95 % for the case of continuous operation.

In general, the biofilter has two behaviours depending on the contaminant charge fed: when loads are low (<20 g $m^{-3}h^{-1}$), the biofilter removal efficiency (for TEX) reaches similar values to the regime "8h ON / 16h OFF". However, when the loads are high (≥ 20 g $m^{-3}h^{-1}$), the biofilter reaches similar elimination capacity to the maximum reached during continuous operation regime (12-13 g $m^{-3}h^{-1}$).

This can be explaining by differences in biodegradation process among the three pollutants:

- Toluene: Surprisingly, the maximum degradation during this period is slightly greater than that obtained during the continuous operation. The maximum removal capacity increased by ≈40 % to reach around 6.5 g $m^{-3}h^{-1}$ (concentration of 0.16 g m^{-3}). This could be explained by the specialization of microbial community in toluene degradation in front of two other compounds (Figure 6.26).
- p-Xylene: Behaviour of p-xylene is similar to that described for the mixture of TEX, reaching the same maximum removal efficiency that in continuous mode (at concentrations 3.0-3.5 g m^{-3} h^{-1}) when high contaminant load are supplied (≥ 8 g m^{-3} h^{-1}) (Figure 6.27).
- Ethylbenzene: suffers a decrease of 35-40 % in maximum elimination capacity (<4.0 g m^{-3} h^{-1}). It seems that, the presence of toluene higher concentrations inhibit ethylbenzene biodegradation (Figure 6.28).

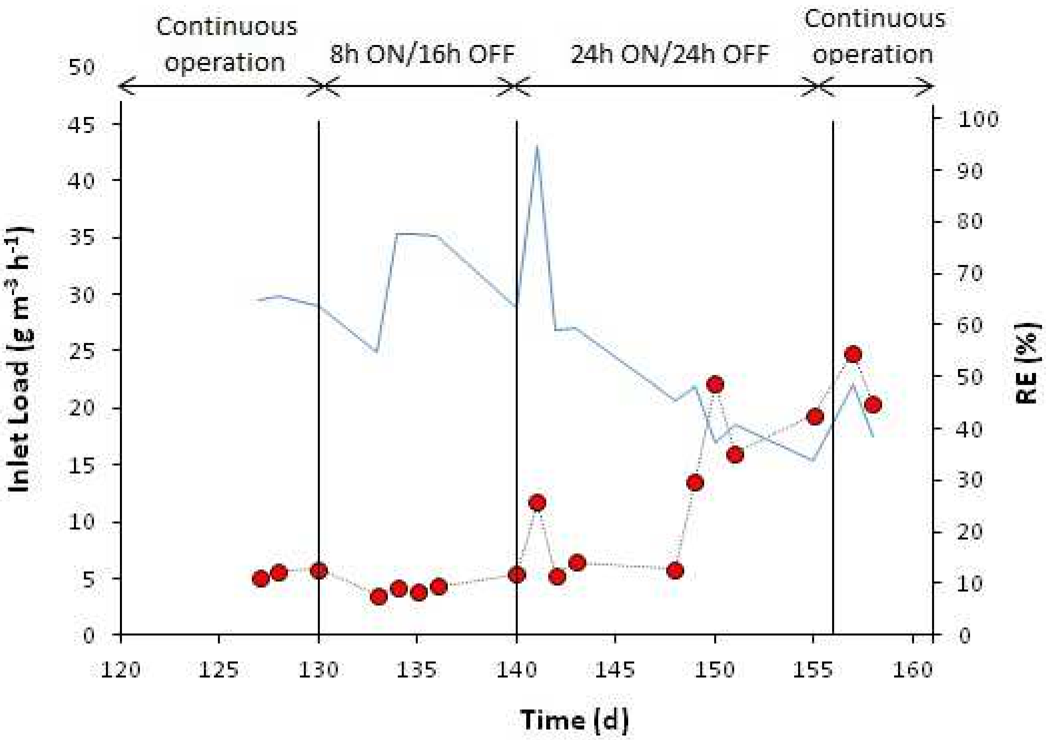


Figure 6.26 Evolution of the toluene inlet load and elimination capacity for BF2 during the intermittent period.

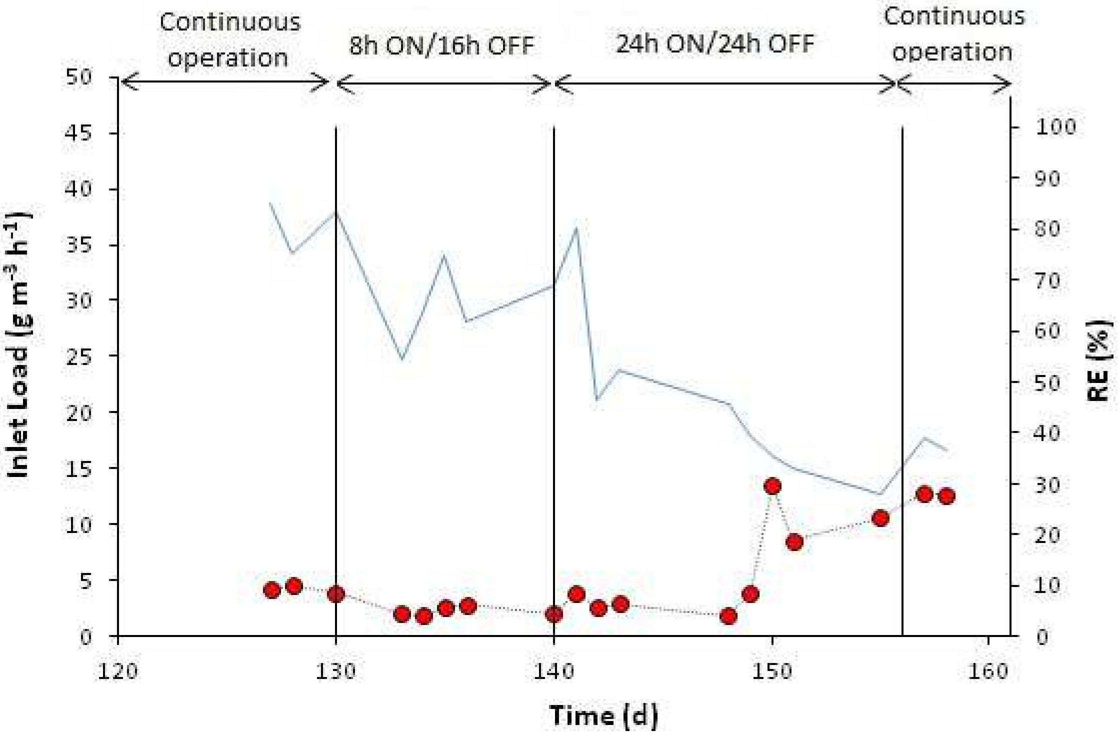


Figure 6.27 Evolution of the p-xylene inlet load and elimination capacity for BF2 during the intermittent period.

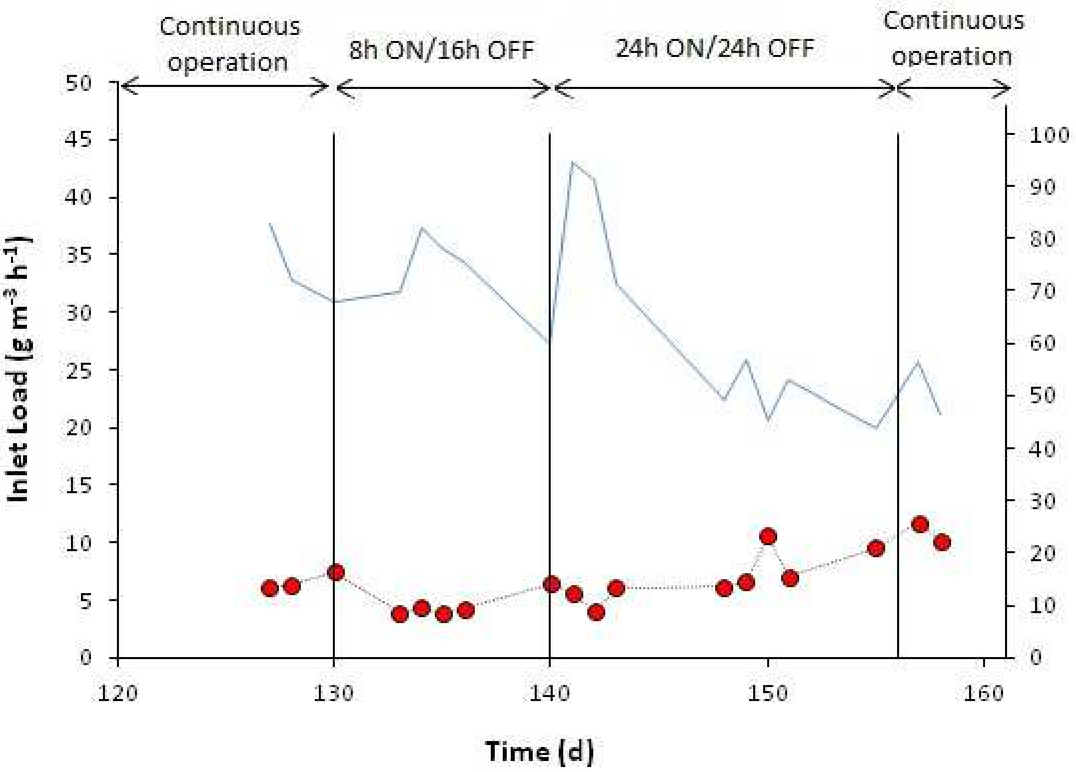


Figure 6.28 Evolution of the ethylbenzene inlet load and elimination capacity for BF2 during the intermittent period.

6.3.4.4. Restoration of continuous regime and operation at higher concentrations (days 156-160).

After testing discontinuous operation, it was decided to apply a continuous regime at high relative concentrations (≈0.75 g m^{-3} to BF1 and ≈1.10 g m^{-3} to BF2) for 5 days before stopping the system. Results obtained in this case are similar at those for BF1. Therefore, regardless of the alternate applied periods ("8h ON / 16h OFF" or "24h ON / 24 OFF"), the biofilter is capable of recovering a good microbial activity at 48h since the restoration of the continuous operation (EBRT < 90 s, contaminant concentrations < 1.0 g m^{-3} and stop time <100 h).

In the literature several examples of disruptions in biofilters' operation are found. Martin and Loehr (1996) treated a contaminated gas stream with toluene, benzene and p-xylene using a biofilter filled with compost, obtaining the following conclusions:

- ✓ The time of re-acclimation after a stop was lower and removal efficiency was greater when, during stop, humid air went through the bed instead of interrupting both the pollutant supply and the humid air supply.
- ✓ The time of re-acclimation after a stop of two weeks was lower than the acclimation period when the biofilter was inoculated. Therefore, after a break in the bioreactor operation, it is advisable to store it for further use instead of refilling with new media.

- ✓ Toluene is the most rapidly pollutant to acclimate and recover from disruptions in supply.

Rene *et al.* (2012) corroborated that removal efficiencies were recovered at 100% after stops of 4 and 7 days in a fungi biofilter filled with perlite and fed with moisture of BTEX. These findings are very similar to those obtained for the BF1 filled with Soil-1.

6.3.5. Secondary parameters

6.3.5.1. Temperature

Changes in temperature were observed in both biodegradation systems (Figures 6.29 and 6.30). Temperature was slightly higher at the output than in the input (ambient temperature) from the beginning of operation in the case of BF1 and from day 28th in the case of BF2, showing that heat released is directly proportional to the extent of microbial degrading activity (the bio-oxidation of organic compounds is an exothermic reaction).

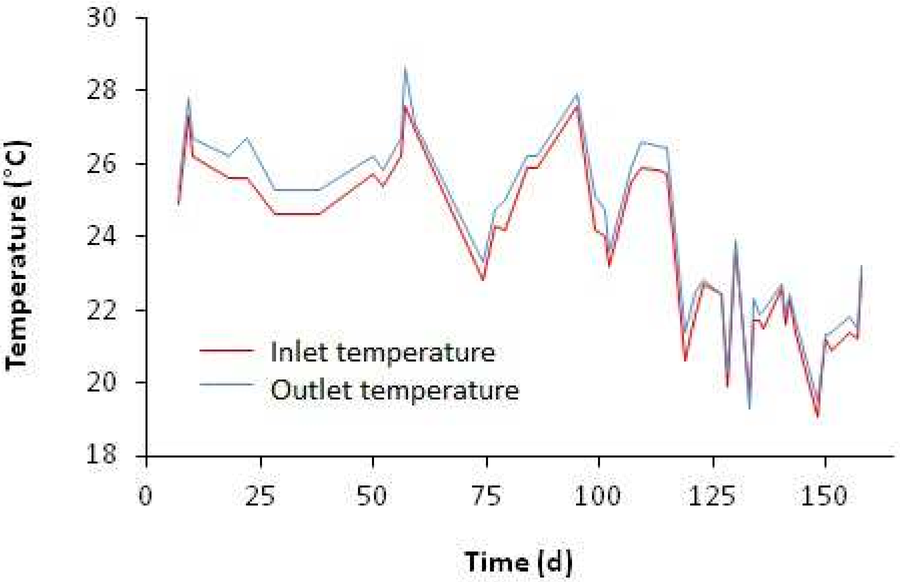


Figure 6.29 Temperature evolution in BF1 during operating time.

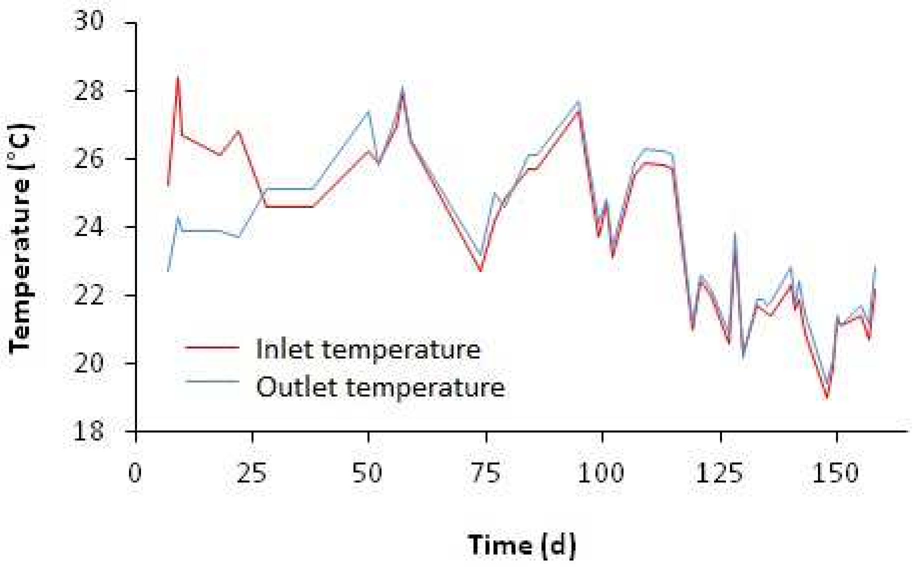


Figure 6.30 Temperature evolution in BF2 during operating time.

6.3.5.2. Carbon dioxide production (CO_2)

Monitoring the CO_2 concentration in the gas phase provided information on biomass activity and the contaminant's mineralization level. There is a correlation between the quantity of carbon dioxide released and the quantity of TEX oxidized determined by the following biochemical reactions (Gallastegui *et al.*, 2011):

$$aC_7H_8 + bO_2 + c(NH_4)HCO_3 \xrightarrow{microorganims} CH_{1.98}O_{0.44}N_{0.18} + dH_2O + eCO_2 \qquad (1)$$

$$fC_8H_{10} + gO_2 + h(NH_4)HCO_3 \xrightarrow{microorganims} CH_{1.98}O_{0.44}N_{0.18} + iH_2O + jCO_2 \qquad (2)$$

In Figures 6.31 and 6.32 biofilters' removal capacity is correlated to CO_2 production for continuous and discontinuous operation regimes. These figures allow checking the stability of the microbial community between different operating periods. In both cases, it can be seen that the relationship between the removal efficiency and the carbon dioxide production is maintained constant despite changes in the operating regime.

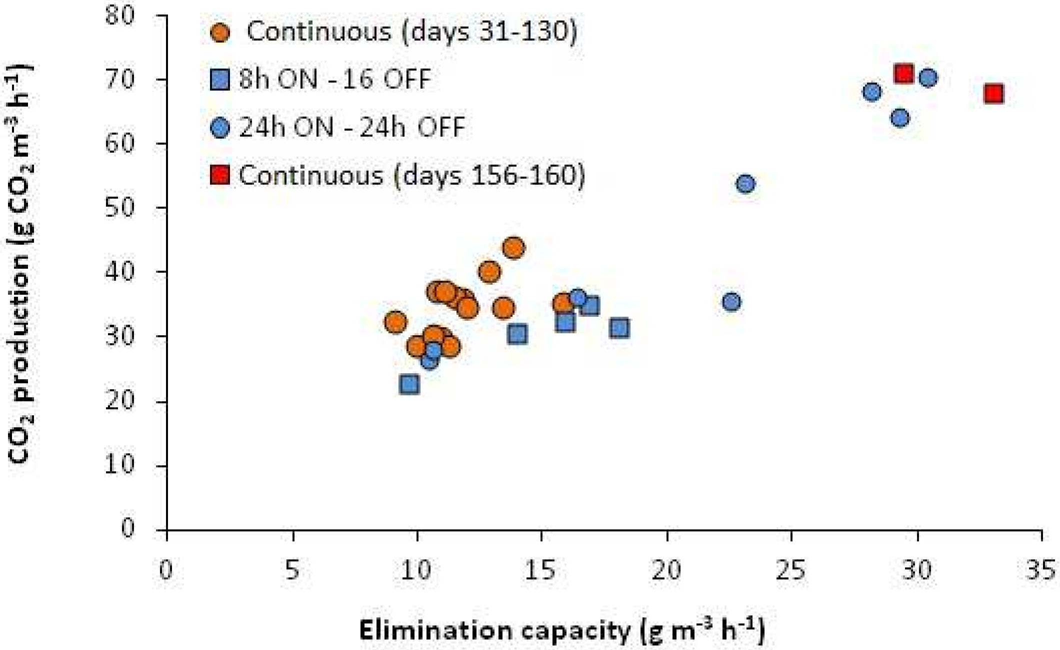


Figure 6.31 Production of CO_2 vs. TEX elimination capacity in BF1

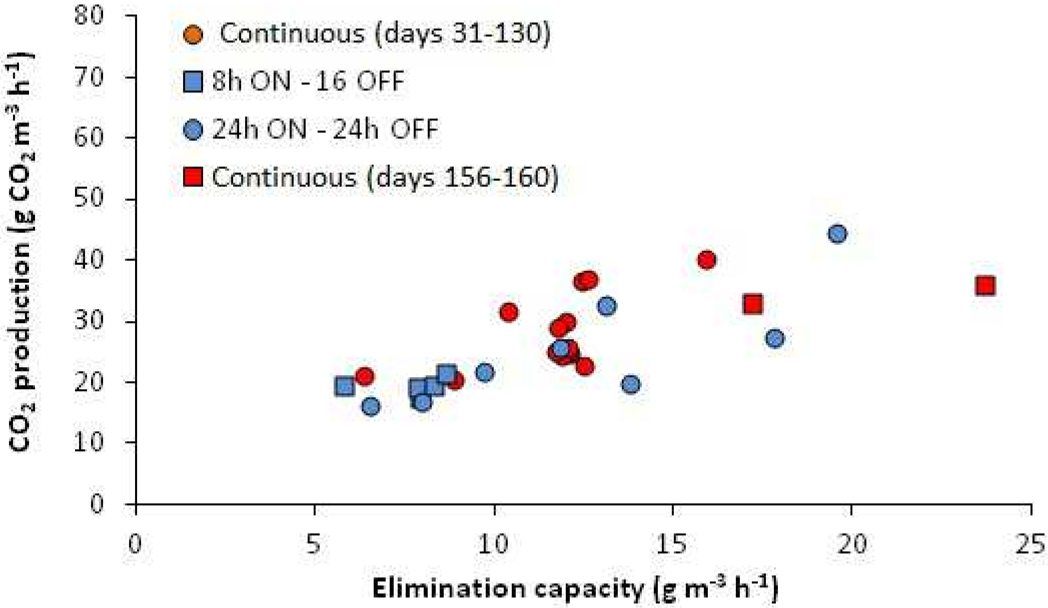


Figure 6.32 Production of CO_2 vs elimination capacity in BF2

6.3.5.3. Irrigation and soil moisture

Evolution of moisture in both supports (Soil-1 and Soil-2) and water irrigation (vertical blue lines) applied throughout the operation period are shown in Figures 6.33 and 6.34. The moisture content of both soils was maintained at similar values. Nevertheless, the addition of water to Soil-1 was more important in front of the quantity added to Soil-2 because during visual controls, the dryness was most notorious in Soil-1 than in Soil-2. This could be explained by the presence of stones similar to lava rock in Soil-2.

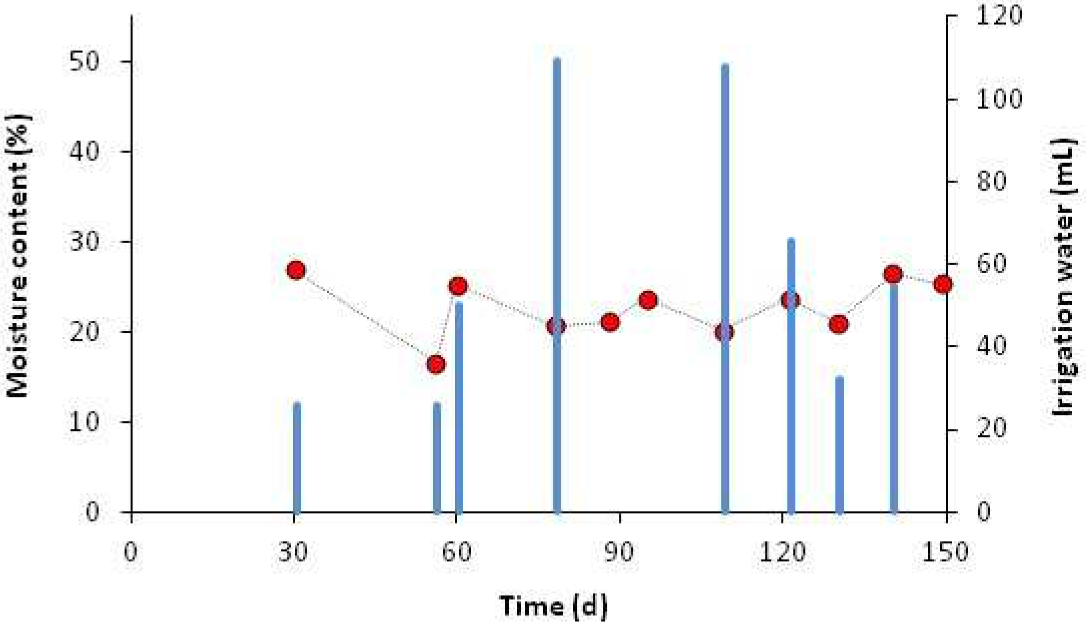


Figure 6.33 Moisture content evolution in the BF1 packed with Soil–1.

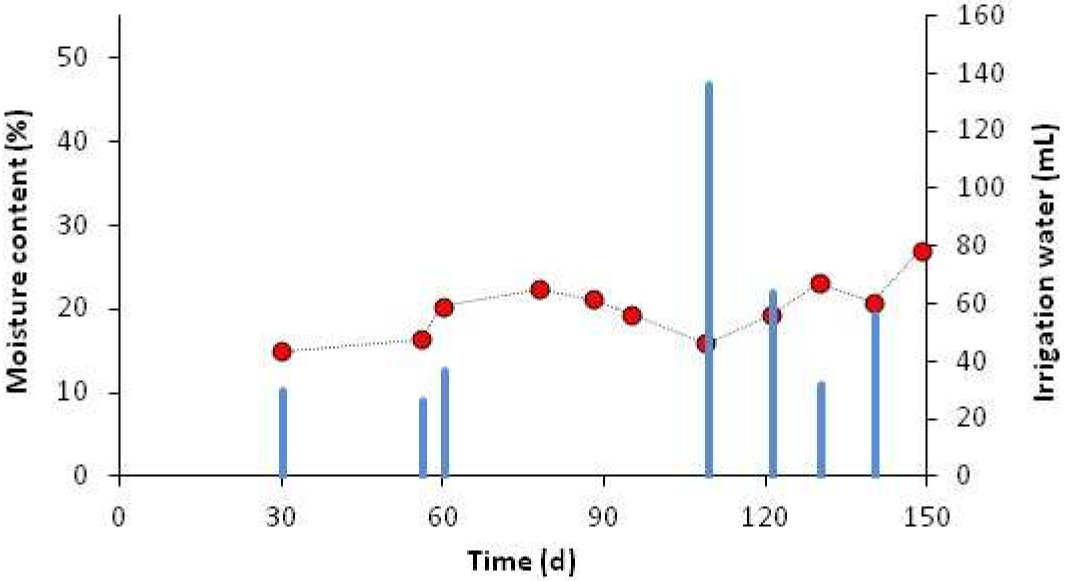


Figure 6.34 Moisture content evolution in the BF2 packed with Soil-2.

6.4. Conclusions

The results concerning wettability indicate that the partial or complete dehydration of the supports is discouraged due to its inability to be wetted from the saturated gas stream and the possibility to acquire hydrophobic properties.

Concerning the adsorption test, Soil-1 is capable of retaining toluene almost twice compared to Soil-2 on its dry surface for the range of studied concentrations. Nevertheless, this capability (≈2 mg of toluene per g of support) is negligible compared to other classical adsorbents (granular activated carbon or zeolites).

Both media, Soil-1 and Soil-2 presented a pressure drop very low in the tests performed under dry conditions, which at first favour their use in biofiltration. It does not happen in trials of flooding, where the vast amount of accumulated water caused a pressure drop of 30 mm H_2O in BF1, which would hinder its application to full scale. In BF2, pressure drop only reaches 8 mm H_2O probably due to the abundance of volcanic rock stones in Soil-2.

With regard to media bulk density, the abundance of rocks in the Soil-2 causes the density of the biofilter packed with this soil (BF2) is greater than that of BF1 (0.9 g cm^{-3} versus 0.7 g cm^{-3}) but this feature of Soil-2 made it more able to keep constant moisture content. High density makes Soil-2 inapt for its application in some places such as roofs. Both soils have higher bulk densities than traditional organic media (compost or peat); nevertheless, their compaction is barely perceptible in 170 days of operation.

According to trials in extreme operating conditions (shutdown periods, changes in EBRT and increase in inlet concentrations), Soil-1 was more suitable for thebiofiltration process compared to the Soil-2. Thus, regardless the resilient periods applied, the BF1 was able to recover the full microbial activity to 48 h since the restoration of continuous operation when EBRT $\geq$ 90 s and contaminant concentration was less than 1.0 g m^{-3}.

References

AFSSET. Agence Française de Sécurité Sanitaire, de l’Environnement et du Travail. 2007. Recommandations pour la qualité de l’air dans les parcs de stationnement couverts. Rapport

Álvarez.Hornos, F.J., Gabaldón, C., Martínez-Soria, V., Martín, M., Marzal, P., Penya-Roja, J.M. 2008. Biofiltration of ethylbenzene vapours: Influence of the packing material. Bioresour. Technol. 99: 269–276.

Álvarez-Hornos F.J., Volckaert D., Heynderickx P.M., Van Langenhove H. 2011. Performance of a composite membrane bioreactor for the removal of ethyl acetate from waste air. Bioresource Technology. 102: 8893-8898.

Anet, B., Couriol, C., Lendormi, T., Amrane, A., Le Cloirec, P., Cogny, G., Fillières, R. 2013. Characterization and selection of packing materials for biofiltration of rendering odourous emissions. Water Air Soil Pollut. 224: 1622–1635

Barona A., Elías A., Cano I., Uriarte A., Artetxe J. 2007. Additional determinations in a potential support material for toluene biofiltration: Adsorption and partition in the nutrient solution. Chemical and Biochemical Engineering Quarterly. 21(2): 151-157.

Bhaskaran, K., Hima, A.M., Haridas, A. 2007. Biofiltration of toluene-contaminated air using an agro byproduct-based filter bed. Appl. Microbiol. Biotechnol. 74: 215–220.

Brady NC, Weil RR. 2002. The Nature and Properties of Soils. 13th Edition, Prentice Hall, Upper Saddle River, NJ, 960 pp., ISBN 0-13-016763-0

Buczynskaa, A.J., Krataa, A. Strangera, M., Locateli, A.F., Kontozova-Deutscha, V., Bencsa, L., Naveaud, I., Roekensd, E., Van Griekena, R. 2009. Atmospheric BTEX-concentrations in an area with intensive street traffic. Atmospheric Environment. 43 (2): 311–318.

COPARLY. 2010. Qualité de l’air dans les parcs de stationnement couverts – Etat des lieux dans 25 parcs de l’agglomération lyonnaise – Synthèse en questions.

Devinny J.S., Deshusses M., Webster T.S. 1999. Biofiltration for Air Pollution Control. Boca Raton, FL, USA: Lewis Publishers.

Delhoménie M.C., Heitz M. 2005. Biofiltration of air: A review. Critical Reviews in Biotechnology. 25: 53–72.

Delhoménie MC., Bibeau L., Gendron J., Brzezinski R., Heitz M. 2003. Degradation of Toluene, Xylene, and Trimethylbenzene Vapors by Biofiltration: A Comparison. Journal of the Air and Waste Management Association. 53(2): 217-226.

Dorado A.D., Lafuente J. Gabriel D., Gamisans X. 2010. The role of water in the performance of biofilters: Parameterization of pressure drop and sorption capacities for common packing materials. J. Hazard. Mater. 180: 693–702.

Dumont E., Andres Y. 2010. Evaluation of innovative packing materials for the biodegradation of H2S: a comparative study. J Chem Technol Biotechnol; 85: 429–43.

Elías A. Barona A., Gallastegui G., Rojo N., Gurtubay L. 2010. Preliminary acclimation strategies for successful start-up conventional biofilters. Air Waste Manage. Assoc. 60(8): 959–967.

Estrada J.M., Kraakman N.J.R., Lebrero R., Muñoz R., 2012. A sensitivity analysis of 511 process design parameters, commodity prices and robustness on the economics of odour 512 abatement technologies. Biotechnology Advances. 30 (6): 1354-1363.

Gallastegui G., Avalos Ramirez A., Elias A., Jones JP., Heitz M. 2011. Performance and macrokinetic analysis of biofiltration of toluene and p-xylene mixtures in a conventional biofilter packed with inert material. Bioresource Technology. 102: 7657–7665.

Gallastegui G., Barona A., Rojo N., Gurtubay L., Elías A. 2013. Comparative response of two organic biofilters treating ethylbenzene and toluene after prolonged exposure. Process Safety and Environmental Protection. 91: 112–122.

Gutiérrez, M.C., Serrano, A., Martín, M.A., Chica, A.F. 2014. Odour in composting processes at pilot scale: monitoring and biofiltration. Environ. Technol. DOI: 10.1080/09593330.2014.880132

Herrygers, H. Van Langenhove, E. Smet. 2000. Biological treatment of gases polluted by volatile sulfur compounds. Environmental Technologies to Treat Sulfur Compounds, IWA Publishing, London. 281–304.

Hoyle FC. 2015. What is soil organic carbon? Department of Agriculture and Food, Western Australia. https://agric.wa.gov.au/n/1364 (Consulted on the fifth august 2015)

Hwang, J.W., Jang, S.J., Lee, E.Y., Choi, C.Y., Park, S. 2007. Evaluation of composts as biofilter packing material for treatment of gaseous p-xylene. Biochem. Eng. J. 35: 142–149.

Juszkiewicz, A. and Kijak B. 2003. Traffic-generated air pollution with volatile organic compounds in Krakôw and its environs. Polish Journal of Environmental Studies. 12(1):49-56.

Kaosol T. and Pongpat N. 2012. Biofilter treating ammonia gas using agricultural residues media. American Journal of Environmental Sciences. 8 (1): 64-70.

Ketterings Q., Reid S., Rao R. 2007. Cation Exchange Capacity (CEC). Cornell University Cooperative Extension. Department of Crop and Soil Sciences, College of Agriculture and Life Sciences, Cornell University. Agronomy Fact Sheet Series # 22.

Kwon, H.M., Yeom, S.H. 2009. Design of a biofilter packed with crab shell and operation of the biofilter fed with leaf mold solution as a nutrient. Biotechnol. Bioeng. Eng. 14: 248–255.

Kuykendall J.R., Shaw S.L., Paustenbach D., Fehling K., Kacew S., Kabay V. 2009. Chemicals present in automobile traffic tunnels and the possible community health hazards: A review of the literature. Inhalation Toxicology. 21(9): 747–792

Lawrence S.J. 2006. Description, properties, and degradation of selected volatile organic compounds detected in ground water — A Review of Selected Literature: Atlanta, Georgia, U. S. Geological Survey. 2006. Open-File Report 2006-1338, 62 p., a Web-only publication at http://pubs.usgs.gov/ofr/2006/1338/. (consulted on April 15th 2015)

Hernández J., Lafuente J., Prado OJ., Gabriel D. 2013. Startup and long-term performance of biotrickling filters packed with polyurethane foam and poplar wood chips treating a mixture of ethylmercaptan, H2S, and NH3. Journal of the Air & Waste Management Association. 63 (4): 462-471.

Lebrero R., Estrada JM., Muñoz R., Quijano G. 2014. Deterioration of organic packing materials commonly used in air biofiltration: Effect of VOC-packing interactions. Journal of Environmental Management. 137: 93-100.

Lebrero R., Rodríguez E., García-Encina PA., Muñoz R. 2011. A comparative assessment of biofiltration and activated sludge diffusion for odour abatement. Journal of Hazardous Materials. 190: 622–630.

Lee M.C., Kim Y.S., Nagajyoti P.C., Park W., Kim K.Y. 2011. Pattern Classification of Volatile Organic Compounds in Various Indoor Environments. Water Air Soil Pollut. 215:329–338.

Li, J.J., Wu, Y.D., Zhang, Y.L., Zeng, P.Y., Tu, X., Xu, M.Y., Sun, G.P. 2014. Emission of odorous volatile organic compounds from a municipal manure treatment plant and their removal using a biotrickling filter. Environ.Technol. DOI: 10.1080/09593330.2014.974679

Maestre J.P., Gamisans X., Gabriel D., Lafuente J. 2007. Fungal biofilters for toluene biofiltration: Evaluation of the performance with four packing materials under different operating conditions, Chemosphere. 67: 684–692.

Martin, F.J., Loehr, R.C. 1996. Effect of periods of non-use on biofilter performance. J. Air Waste Manage. Assoc. 46: 539–546.

Mathur, A.K., Majumder, C.B., Chatterjee, S. 2007. Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media. J. Hazard. Mater. 148: 64–74.

McGaughey, G. R., Desai N.R., Allen D.T., Seila R.L., Lonneman W.A., Fraser M.P., *et al.* 2004. Analysis of motor vehicle missions in a Houston tunnel during the Texas Air Quality Study 2000. Atmospheric Environment. 38: 3363-3372.

Miller C. 2000. Understanding the Carbon-Nitrogen Ratio. 30 (4).

Mudliar, S.N., Giri, B.S., Padoley, K.V., Satpute, D., Dixit, R., Bhatt, P., Pandey, R.A., Juwarkar, A., Vaidya, A.N. 2010. Bioreactors for treatment of VOCs and odours – A review. J. Environ. Manage. 91, 1039 – 1054.

Na K. 2006. Determination of VOC source signature of vehicle exhaust in a traffic tunnel. Journal of Environmental Management. 81: 392–398.

NHMRC-National Health and Medical Research Council. 2008. Air Quality and Around Traffic Tunnels. Final Report. Australia.

Nikiema, J., Dastous, P.A., Heitz, M. 2007. Elimination of volatile organic compounds by biofiltration: a review. Rev. Environ. Health. 22 (4), 273 – 293.

Ondarts M, Hort C, Sochard S, Platel V, Moynault L, Seby F. 2012. Evaluation of compost and a mixture of compost and activated carbon as biofilter media for the treatment of indoor air pollution. Environmental Technology. 33(3):273-284

Ortiz, I., Revah, S., Auria, R. 2003. Effect of packing material on the biofiltration of benzene, toluene and xylene vapours. Environ. Technol. 24, 263 – 275.

Pérez, M.C., Álvarez-Hornos, F.J., Portune, K., Gabaldón, C. 2015. Abatement of styrene waste gas emission by biofilter and biotrickling filter: comparison of packing materials and inoculation procedures. Appl. Microbiol. Biotechnol. 99: 19–32.

Quinlan, C., Strevett, K., Ketcham, M., Grego, J. 1999. VOC Elimination in a compost biofilter using a previously acclimated bacterial inoculum. J. Air Waste Manage. Assoc. 49: 544–553.

Rani, M., Sattler M.L. 2011. Removal of propylene and butylene as individual compounds with compost and wood chip biofilters. J. Air Waste Manage. Assoc. 61: 527–534.

Rene, E., Mohammad, B.T., Veiga, M.C., Kennes, C. 2012. Biodegradation of BTEX in a fungal biofilter: Influence of operational parameters, effect of shock-loads and substrate stratification. Bioresour. Technol. 116: 204–213.

Rondeau A., Mandon A., Malhautier L., Poly F., Richaume A. 2012. Biopurification of air containing a low concentration of TEX: comparison of removal efficiency using planted and non-planted biofilters. J. Chem. Technol. Biotechnol. 87: 746–750

Sattler ML, Garrepalli DR, Nawal CS. 2009. Carbonyl sulfide removal with compost and wood chip biofilters, and in the presence of hydrogen sulfide. J Air Waste Manag Assoc. 59(12):1458-67.

Singh RS., Agnihotri SS., Upadhyay SN. 2006. Removal of toluene vapour using agro-waste as biofilter media. Bioresource Technology. 97: 2296–2301.

Son HK. 2008. Pilot-Scale Compost Media Biofilter Treatment Of Volatile Organic Compounds. Compost Science & Utilization. 16 (2): 83-89.

Song JH, Ramirez J, Kinney KA. 2003. Nitrogen utilization in a vapor-phase biofilter. Water Research. 37: 4497–4505

Sun, Y., Quan, X., Chen, J., Yang, F., Xue, D., Liu, Y., Yang, Z., 2002. Toluene vapour degradation and microbial community in biofilter at various moisture content. Process Biochemistry. 38: 109-113.

Swanson W.J. and Loehr R.C. 1997. Biofiltration: Fundamentals, design and operation principles, and applications. Journal of Evironmental Engineering. 123 (6) : 538-546

United States Department of Agriculture. 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd edition. Natural Resources Conservation Service. U.S. Department of Agriculture Handbook 436.

United States Department of Agriculture. 1999. Soil mechanics level I. Module 3-USDA Textural Soil Classification. Study guide. Soil conservation service.

Van Lith C, Leson G & Michelsen R. 1997. Evaluating design options for biofilters. J. Air Waste Manage. Assoc. 47: 37–48.

Viswanathan, S., Neereckal, G., Buyuksonmez, F. 2013. Removal of beta-pinene and limonene using compost biofilter. J. Air Waste Manage. Assoc. 63: 237–245.

Wani, A.H., Lau, A.K., Branion, R.M.R. 2000. Performance of compost and hog-fuel biofilters: impact of periods of non-use and varying methyl mercaptan loading. Environ. Technol. 21: 271–283.

Wu, D., Zhang, C., Geng, C., Hao, L., Quan, X. 2009. Removal of multicomponent VOCs in off-gases from an oil refining wastewater treatment plant by a compost-based biofilter system. Front. Environ. Sci. Engin. China. 3: 483–491.

Yang, L., Wang, X., Funk, T.L., Gates, R.S. 2011. Biofilter media characterization and airflow resistance test. Transactions of the ASABE. 54: 1127–1136

Appendix 6A. Detailed characterization of Soil-1 and Soil-2

Table 6.A1 Physico-chemical properties of Soil-1

Parameters	Value	Method	Unity
Moisture (iao-01)	19.4	Gravimétrico	% (smo)
pH (in water 1/25) (iao-02)	9.0	Potenciométrico	upH (smo)
Neutralization potential	9.48	Norma UNE EN 12945:2008	Kg CaO/100Kg (smo)
Conductivity (water 1/25)(iao-03)	0.13	Conductimétrico	dS/m (smo)
Total organic matter(iao-05)	5.29	Calcinación	% P/P (sms)
Total Nitrogen (iao-06)	0.18	Kjeldahl	% de N P/P (sms)
Organic Nitrogen (iao-06)	0.16	Kjeldahl	% de N P/P (sms)
Ammoniacal Nitrogen (iao-06)	0.00	Kjeldahl	% de N P/P (sms)
Relation C/N	14.59	Cálculo	
Total Anhydride Phosphorous (iao-07)	0.35	Gravimétrico	% de P_2O_5 P/P (sms)
Total Potassium Oxide (iao-08)	0.45	Fotometría de llama	% de K_2O P/P (sms)
Total Sodium Oxide (iao-08)	0.67	Fotometría de llama	% Na_2O P/P (sms)
Total Calcium Oxide (iao-08)	1.77	Absorción atómica	% de CaO P/P (sms)
Total Magnesium Oxide (iao-08)	1.40	Absorción atómica	% de MgO P/P (sms)
Total Iron (iao-08)	22600	Absorción atómica	mg de Fe/Kg (sms)
Total Manganese (iao-08)	602	Absorción atómica	mg de Mn/Kg (sms)
Total Cupper (iao-08)	44	Absorción atómica	mg de Cu/Kg (sms)
Total Zinc (iao-08)	65	Absorción atómica	mg de Zn/Kg (sms)
Total humic extract (iao-09)	1.48	Oxidación con Dicromato	% P/P (sms)
Humic acids	1.24	Ataque ácido y oxidación con Dicromato	% P/P (sms)
Fulvic acids	0.25	Ataque ácido y oxidación con Dicromato	% P/P (sms)
Cation-exchange capacity	15.5	Absorción atómica	meq de Na/100g (sms)

Table 6.A2 Physico-chemical properties of Soil-2

Parameters	Value	Method	Unity
Moisture (iao-01)	2.5	Gravimétrico	% (smo)
pH (in water 1/25) (iao-02)	7.0	Potenciométrico	upH (smo)
Neutralization potential	13.10	Norma UNE EN 12945:2008	Kg CaO/100Kg (smo)
Conductivity (water 1/25)(iao-03)	0.03	Conductimétrico	dS/m (smo)
Total organic matter(iao-05)	4.26	Calcinación	% P/P (sms)
Total Nitrogen (iao-06)	0.04	Kjeldahl	% de N P/P (sms)
Organic Nitrogen (iao-06)	0.03	Kjeldahl	% de N P/P (sms)
Ammoniacal Nitrogen (iao-06)	0.00	Kjeldahl	% de N P/P (sms)
Relation C/N	59.33	Cálculo	
Total Anhydride Phosphorous (iao-07)	0.49	Gravimétrico	% de P_2O_5 P/P (sms)
Total Potassium Oxide (iao-08)	0.13	Fotometría de llama	% de K_2O P/P (sms)
Total Sodium Oxide (iao-08)	0.50	Fotometría de llama	% Na_2O P/P (sms)
Total Calcium Oxide (iao-08)	1.33	Absorción atómica	% de CaO P/P (sms)
Total Magnesium Oxide (iao-08)	2.16	Absorción atómica	% de MgO P/P (sms)
Total Iron (iao-08)	29850	Absorción atómica	mg de Fe/Kg (sms)
Total Manganese (iao-08)	544	Absorción atómica	mg de Mn/Kg (sms)
Total Cupper (iao-08)	56	Absorción atómica	mg de Cu/Kg (sms)
Total Zinc (iao-08)	60	Absorción atómica	mg de Zn/Kg (sms)
Total humic extract (iao-09)	1.9	Oxidacion con Dicromato	% P/P (sms)
Humic acids	1.24	Ataque ácido y oxidación con Dicromato	% P/P (sms)
Fulvic acids	0.66	Ataque ácido y oxidación con Dicromato	% P/P (sms)
Cation-exchange capacity	7.7	Absorción atómica	meq de Na/100g (sms)

Appendix 6B. Elimination capacity vs Inlet Load

Figures 6.B1 to 6.B3 show the elimination capacity on the BF1 in front of the inlet load of toluene, p-xylene and ethylbenzene, respectively.

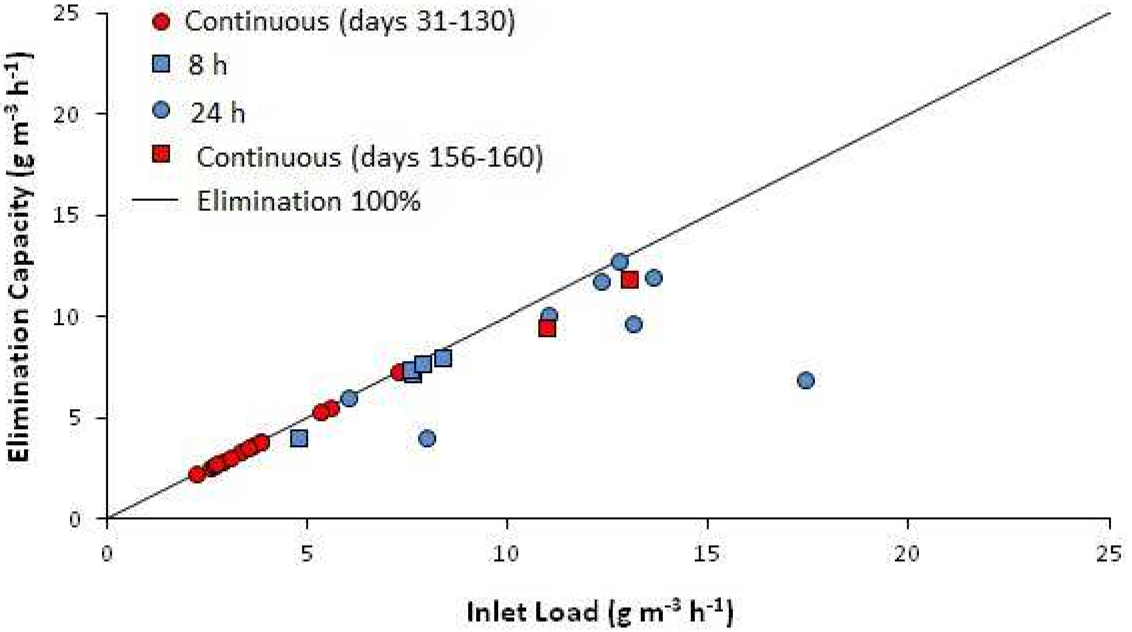


Figure 6.B1. Inlet load vs. elimination capacity for the toluene in BF1.

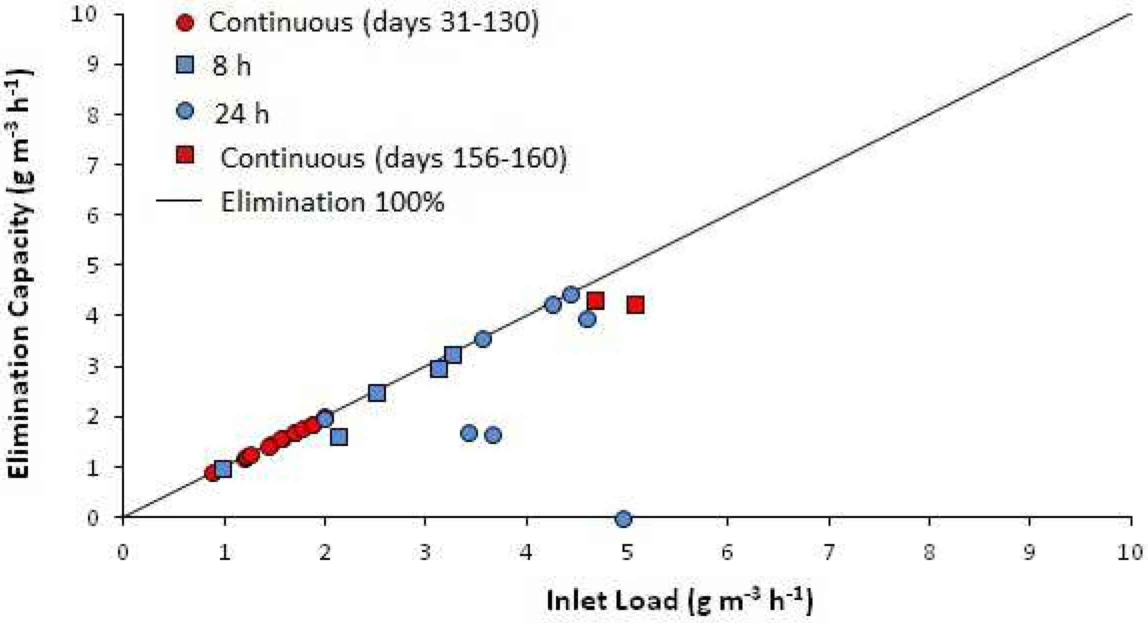


Figure 6.B2. Inlet load vs. elimination capacity for the p-xylene in BF1.

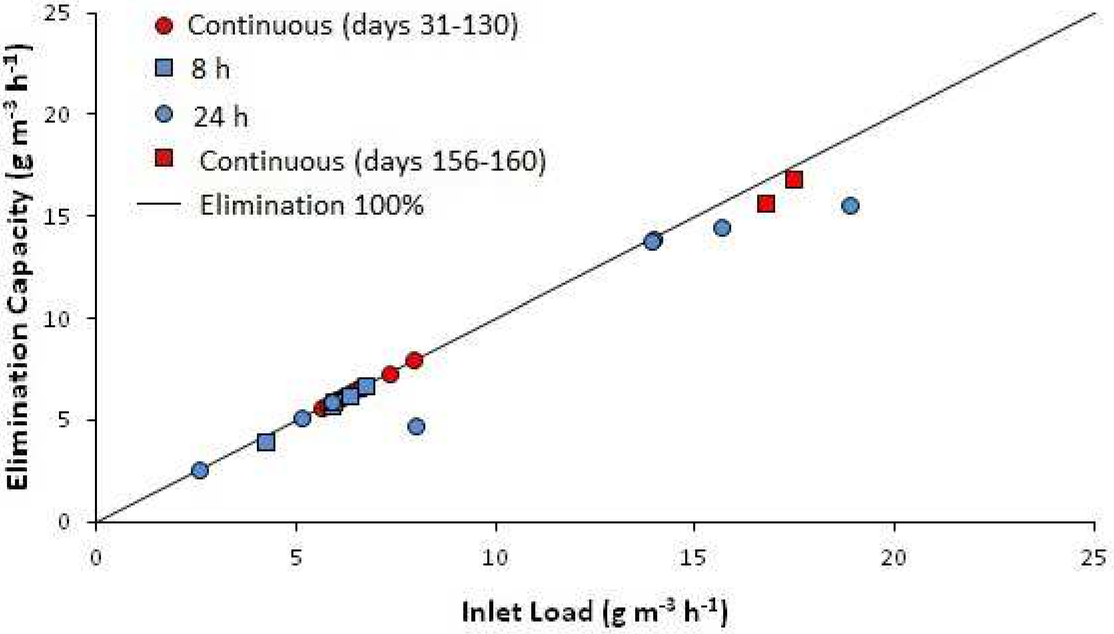


Figure 6.B3. Inlet load vs. elimination capacity for the ethylbenzene in BF1.

Figures 6.B4 to 6.B6 show the elimination capacity on the BF2 in front of the inlet load of toluene, p-xylene and ethylbenzene, respectively.

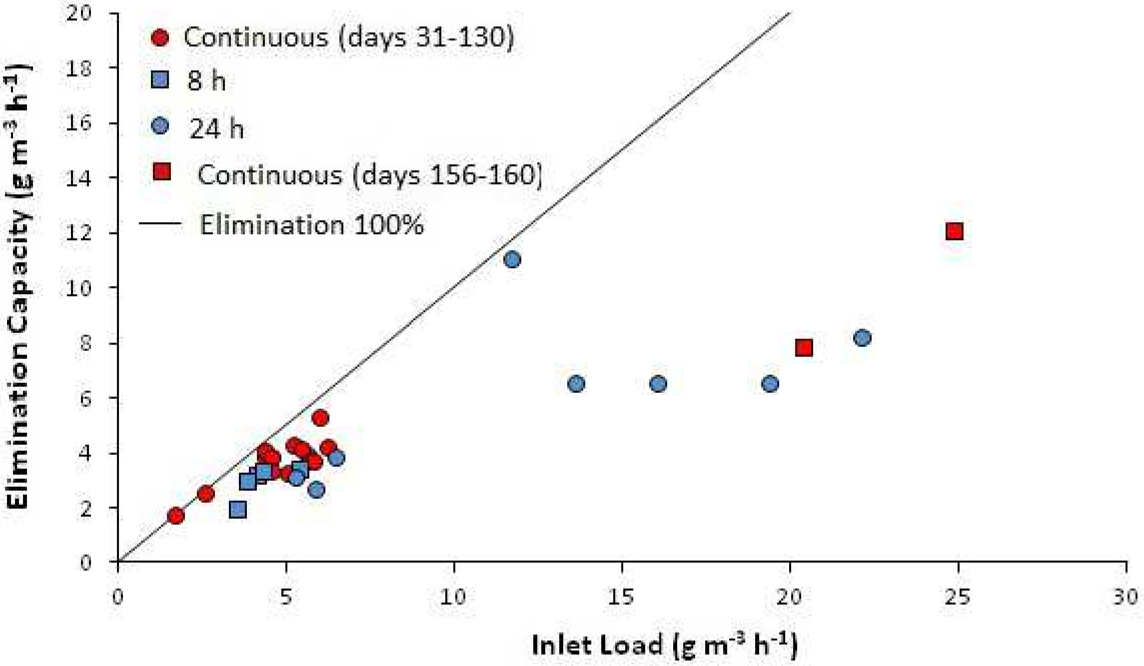


Figure 6.B4. Inlet load vs. elimination capacity for the toluene in BF2.

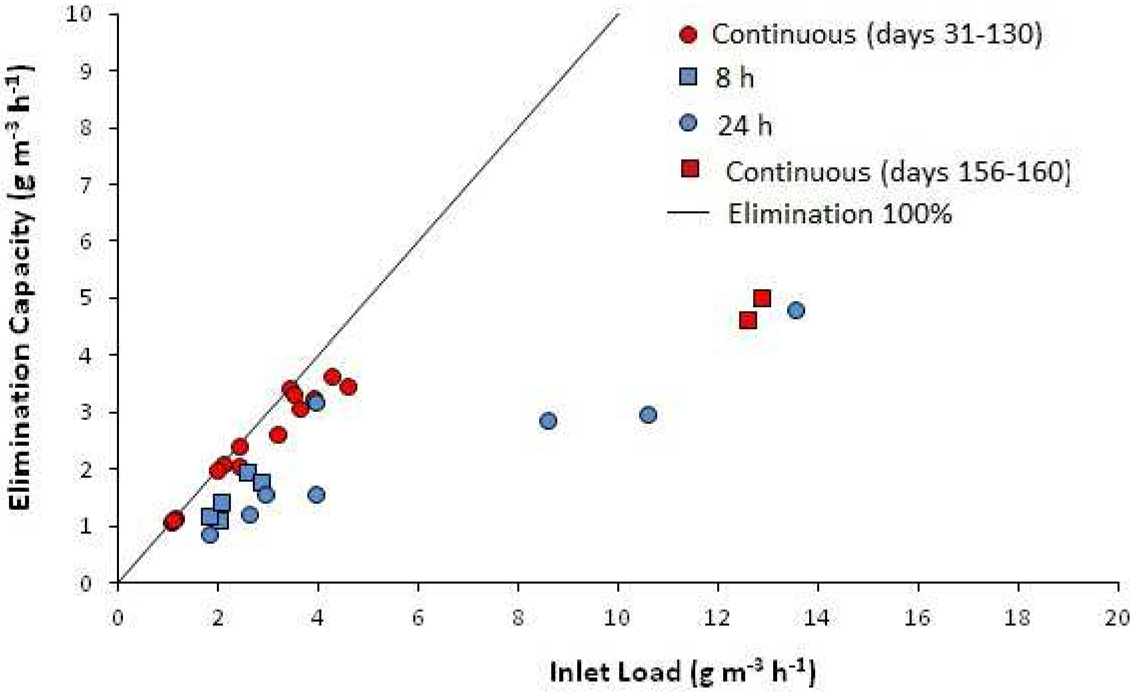


Figure 6.B5. Inlet load vs. elimination capacity for the p-xylene in BF2.

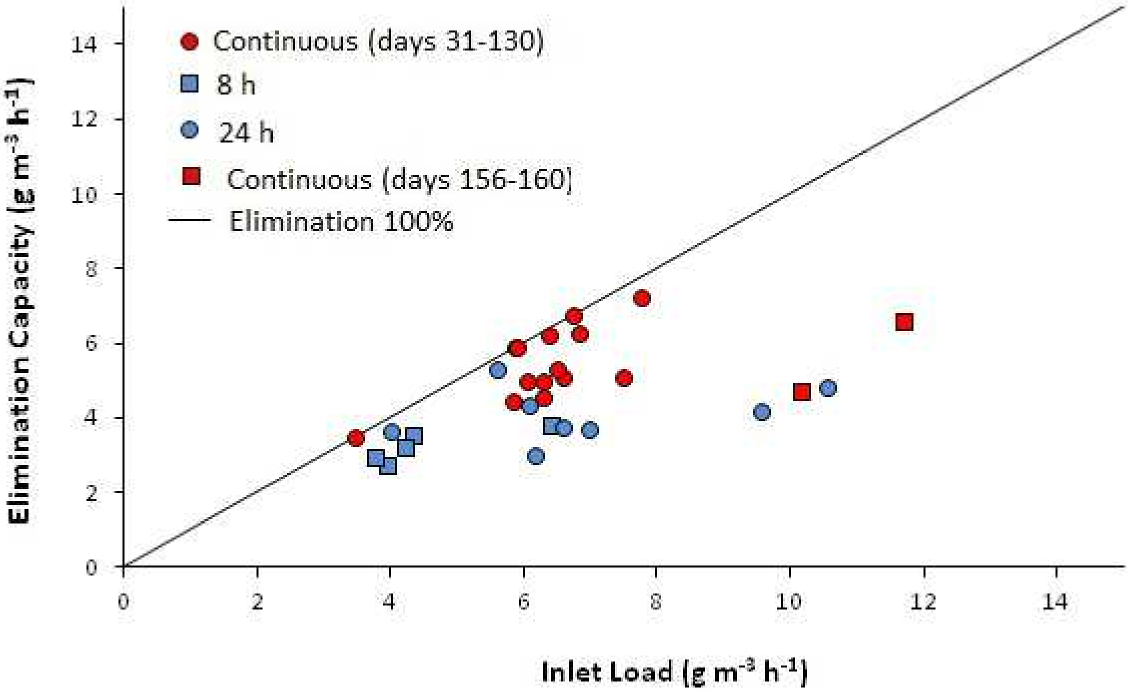
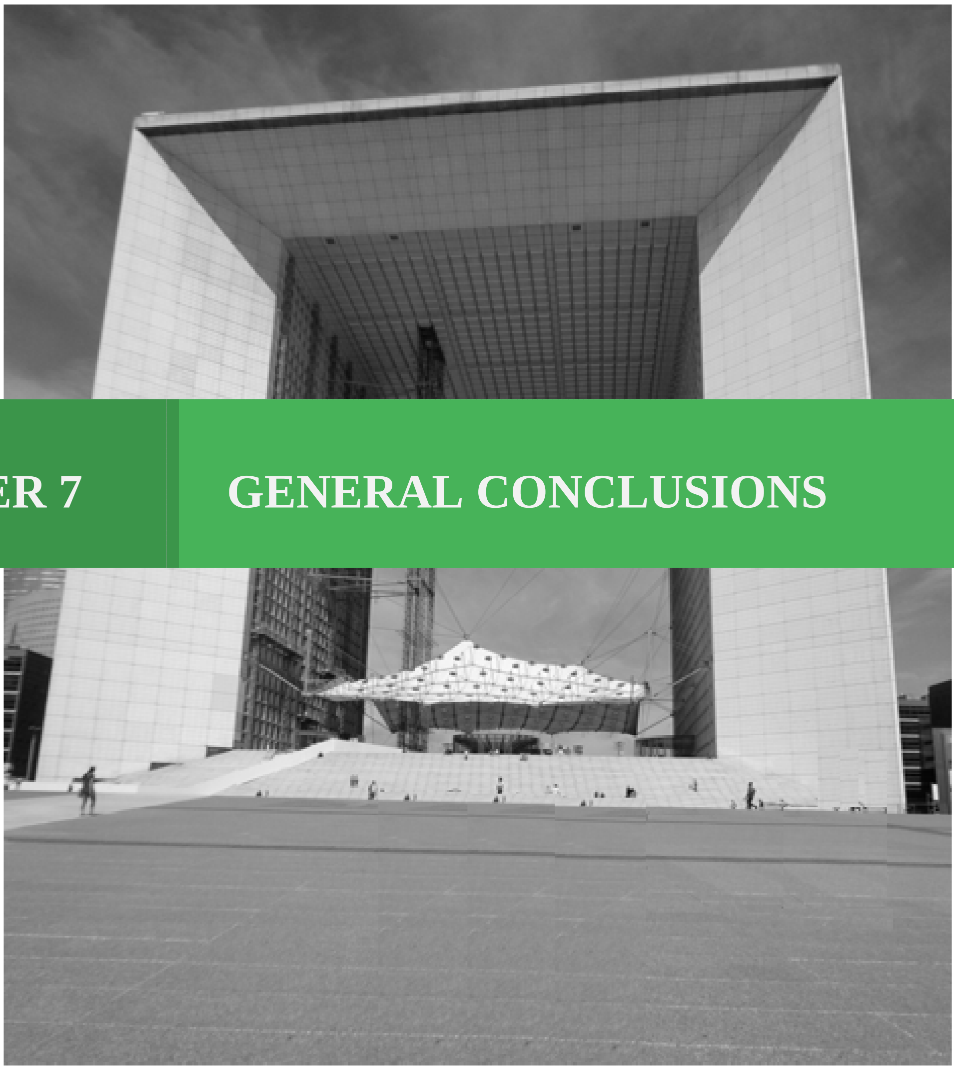


Figure 6.B6. Inlet load vs. elimination capacity for the ethylbenzene BF2.



CHAPTER 7

GENERAL CONCLUSIONS

7. GENERAL CONCLUSIONS

The number and type of chemical compounds identified and quantified indoors have been continuously increasing over the last few years, and the diversity in their physico-chemical properties makes their treatment difficult despite the very low concentrations at which they are present. In this context, most of the researches on indoor air treatment have been applied to several technologies for contaminant degradation at ppm levels, whilst ppb concentrations are measured in indoor air. These researches are predominantly focused on the contaminants' removal and less in their secondary impacts.

Several conventional and innovative technologies for indoor air pollution were herein presented (Chapter 3). Biological treatment systems such as biofiltration are between these alternatives. In order to overcome many of the drawbacks of the different technologies, hybrid systems have been proposed, such as the plasma+catalytic hybrid system, adsorption+photocatalysis hybrid system, and biological process+adsorption hybrid system. This last proposal was implemented and studied (Chapters 4 and 5) as the hybrid technologies seem to be the best option to treat the variety of indoor pollutants.

The efficiencies of a biofiltration technology and a hybrid system consisting on the combination of biofiltration and adsorption in the treatment of indoor air pollution were compared (Chapter 4). It was proved that even at low concentrations (2-45 ppb for toluene and 1-33 ppb for p-xylene) biofiltration was able to achieve high removal efficiencies for the target pollutants (100% for toluene and up to 98% for p-xylene) at low EBRT (23 s). Toluene was more easily degraded than p-xylene by biofiltration, reaching higher values of removal efficiency throughout the experimental tests. Nevertheless, the results highlight the potential of the hybrid system as this showed that at very low EBRT (7.7s), which implies saving space, biodegradation still has high removal efficiencies (82% in average for toluene and 49% for the p-xylene). These removal efficiencies were improved by the presence of the subsequent adsorption step. Accordingly, the HS was the most robust in front of the heterogeneity of indoor pollutants and operational disruptions. Additionally, the AC stage ensured the treatment of bio-by-products which were only detected in BF system.

On the other hand, acclimation of the biofiltration packing material seems to be necessary. In fact, in the present study, acclimation period was effectively reduced (almost in a factor of 3) after the inoculation of the compost with an aerobic activated sludge and the exposure of this to higher pollutant concentrations than those found in indoor environments.

The effectiveness of the hybrid system was also tested in the treatment of a toluene micro polluted effluent (concentrations from 17 to 52 $\mu g\ m^{-3}$), undergoing peaks of concentration close to 733 $\mu g\ m^{-3}$ during a few hours every day (2-3h) (Chapter 5). Removal efficiency of the biofilter step was very high (near 100%) during stable concentrations, but it was sensitive to rapid changes in pollutant inlet loads that varied from 4.2 10-3 to 0.20 g m^{-3} h^{-1}. Nevertheless, the adsorption column placed downstream biofiltration was able to positively manage the toluene concentration peaks.

Special confined environments with high concentration levels due to vehicular traffic were also considered (Chapter 6). The feasibility of re-using two soils recovered from construction sites as the media in a biological system for the treatment of this pollution was proved. These soils were completely characterized and used each one in two lab-scale biofilters to treat a mixture of toluene, ethylbenzene and p-xylene at concentrations of 27-152ppm, 15-107 ppm, and 8-81 ppm, respectively. These contaminants were chosen as they are generated by vehicular combustion engines. Biofilters resilience was studied under progressive increases in pollutant loading and operational alternate periods. Soil-1 was stood out to be more suitable for biological processes because of its absorption capacity, low pressure drop and its ability to recover from changes in operating conditions.

Finally, the research raises important questions about the emissions of both HS and BF systems in indoor environments. The assessment of by-products and particles generation by the biofilter and the hybrid systems was carried out. Results suggest that both HS and BF systems released particles in the range of ultrafine particles, $PM_{2.5}$ and PM_{10}.

In brief, the promising results presented in this research suggest that it would thus be of interest to carry out other studies in order to:

- Measure particle emissions in a larger size range and in a larger period of time in order to compare with guidelines (values for 24h).
- Implement a filter at the end of the treatment process in order to reduce particle emissions.
- Quantify the pressure drop over longer periods of time and with the filter stage.
- Control of air humidity at the outlet of the systems as this parameter greatly influences the quality of indoor air.
- Analyze and quantify the release of microorganisms.
- Optimize the ratio of biofiltration and adsorption treatment in the hybrid system in order to reduce the space requirements.