Biological technologies for the removal of VOCs, odours and greenhouse gases

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ABSTRACT

Biotechnologies for polluted gas treatment have been demonstrated as a very convenient strategy both from the point of view of removal efficiencies but also taking into account economic and environmental indicators, especially conventional biofilters and biotrickling filters. A significant number of studies both at lab, pilot and full-scale have been reported along last decade showing the feasibility of bioreactors for many different gaseous pollutants, even those more hydrophobic, for which new strategies are still under evaluation in order to optimise the process. These technical improvements, together with the need of the development of more cost-efficiency technologies and the increasing awareness of our society about problems related with gaseous emissions (VOCs, odours, GHGs, etc.) show a good perspective to continue with the development and the implementation of these technologies for the abatement of gaseous pollutants in the present and the coming years.

Keywords: VOCs, odours, GHGs, biofiltration, biotrickling filter, gaseous emissions

INTRODUCTION

Atmospheric pollution has traditionally received less attention than other forms of pollution such as soil or water contamination. Volatile organic compounds (VOCs), malodorous emissions and non-CO_2 greenhouse gases are responsible for some of the major air pollution problems in the 21st century. These compounds are emitted from a wide range of activities including industry, waste management, livestock facilities or agriculture.

In the case of wastewater treatment plants (WWTPs), gaseous emissions include numerous inorganic and volatile organic compounds (VOCs) generated along the different operation units of the treatment process. In the case of VOCs, although accurate emission rates are not commonly reported (very likely because of the difficulty of their detection), their relevance is out of question and some estimations quantify them up to 40% of the organic loading fed to industrial or municipal wastewater plants (Bianchi & Varney, 1997). In addition, many of these substances have been identified as a source of odour complaints, such as those containing sulphur, volatile fatty acids, amines, etc. and there is a high number of evidences that indicate that odours constitute an important and increasing issue in WWTPs. Therefore, gaseous effluents from WWTPs constitute not only a health concern for the plant operators but also a potential nuisance for the surrounding residential areas. In this sense, there is an increasing concern in the public opinion about the hazards caused by these emissions (leading to an increasing number of public complaints), which has caused the emergence of specific legislation for atmospheric pollution control (Lebrero et al., 2011).

Apart from wastewater treatment plants, odorous emissions originate from a wide variety of industrial and waste treatment processes, such as paper mills, refineries, solid waste treatment etc. (Revah & Morgan-Sagastume, 2005). These odorous emissions are complex and variable mixtures of organic and inorganic chemical compounds (Iranpour et al., 2005; Zarra et al., 2008) mainly composed of sulphur compounds (H_2S in concentrations ranging from 5 to 100 ppm_v and mercaptans), volatile organic compounds (fatty acids, aromatic compounds, aliphatic and chlorinated hydrocarbons, terpenes, aldehydes and ketones, etc.), and ammonia and nitrogen derivates (amines, indole, etc.). As indicated in the case of VOCs, an accurate characterization of odorous emissions is extremely difficult, not only because of the high diversity of compounds present, but also because of their extremely low concentrations, usually in the $\mu g\ m^{-3}$ range. Although odorous emissions are neither toxic nor a direct cause of disease, they can affect the quality of life, having a negative effect on human health (Zarra et al., 2008).

Table 1 shows the main compounds reported in WWTPs gaseous emissions. Some of them can represent an important odour problem due to the extremely low detection threshold (e.g. sulphur compounds), but there are other hazardous VOCs such as benzene, toluene or formaldehyde, among others, which can be toxic, mutagenic or carcinogenic.

Moreover, there are still more challenges associated with WWTP volatile emissions apart from VOCs and odour compounds, as it is the case of greenhouse gases (GHG). Indeed, with the information available up to now it is known that the emissions of two important GHGs, such as methane and nitrous oxide, are also relevant in these facilities (Kampshreur et al., 2009). Methane is a powerful GHG (21–25 times more detrimental to the environment than CO_2) that originates from multiple sources, whose atmospheric concentration has increased by 143% over the last 250 years, largely due to increasing emissions from anthropogenic sources. The Intergovernmental Panel on Climate Change (IPCC) has estimated that slightly more than half of the current methane flux to the atmosphere is anthropogenic, from human activities such as agriculture, fossil fuel use, and waste disposal (IPCC, 2007). Methane emissions by source in the United States have been inventoried since 1990, with emissions from WWTPs in 2010 accounting for up to 16.3 Tg CO_2 equivalents (2.5 % US methane emissions). WWTPs constitute one of the most important sources not related with energy industrial activities (petroleum, gas and coal) together with the emissions derived from landfills and manure management (US EPA, 2012). Recently, methane emissions from a full-scale anaerobic/anoxic/oxic (A/A/O) WWTP in China were investigated during spring and summer. The total annual fluxes of CH_4 emissions were $1.69 \cdot 10^4$ kg CH_4 yr^{-1}, while the emission factor per capita was 11.3 g CH_4 $person^{-1}$ yr^{-1} (Wang et al., 2011).

Table 1. *Detection threshold and typical concentration range of the VOCs emitted from WWTPs and their odour relevance (Zarra et al., 2008).*

Odorous compound	**Human detection threshold (ppm)**	**Concentration range (mg m^{-3})**
	Sulphur compounds	
Hydrogen sulphide	0.0005	0-40
Ethyl mercaptan	0.00001	-
Dimethyl sulphide	0.001	-
Dimethyl disulphide	0.000026	0.21
	Nitrogen compounds	
Ammoniac	0.038	-
Trimethyl amine	0.0004	-
Indole	0.0001	-
Scatole	0.001	-
	Volatile Fatty Acids (VFA)	
Acetic acid	1.1	0.06
Butiric acid	0.0003	-
Isovaleric acid	0.0006	-
Propionic acid	0.028	-
	Ketones	
Butanone	0.25	4.5
Acetone	20	0.46
Methyl ethyl ketone	0.25	-
	Aldehydes	
Acetaldehyde	0.0001	-
Propionaldehyde	0.011	-
Valeraldehyde	0.028	-
	Hydrocarbons	
Toluene	2.1	0.5
Benzene	1.4	0.02
Phenol	46	-
Styrene	0.047	-

Treatment strategies

The optimum selection of a technology for a specific odour problem must take into account the abatement efficiency required, the type of source and emitted compounds, the nature and concentration of the compounds, the emission flow rate and both its investment and operating costs (Estrada et al. 2012). Treatment technologies for gaseous effluents are usually classified according to their underlying principles into physical-chemical and biological techniques. Generally, physical methods such as absorption, adsorption or concentration techniques remove the compounds without further destruction by phase transfer, whereas incineration, chemical or photochemical oxidation and biological oxidation result in a partial or total pollutant destruction.

Industrial off-gas emissions have been conventionally treated by physical-chemical techniques such as adsorption, scrubbing, condensation or oxidation processes, despite their high operational costs (associated to their high energy and chemical requirements) and the formation of toxic by-products (derived from incomplete combustions, hazardous liquid effluents from chemical scrubbers, etc.).

Physical-chemical processes are the most suitable technologies when low flow rates with high pollutant concentrations must be treated due to their high efficiency and recovery potential under this particular scenario (Cárdenas-González et al., 2003). However, they are not cost-efficient when the emission flow rates are high and the pollutant concentrations low.

BIOTECHNOLOGIES FOR THE TREATMENT OF GASEOUS EMISSIONS

In the last few decades, conventional treatment systems based on physical-chemical methods have been replaced by their biological counterparts (biofilters, bioscrubbers, biotrickling filters or diffused activated sludge systems). For instance, in 1994, 78% of the waste gas treatment techniques employed in Germany were biological (Frechen, 1994). These technologies have shown high efficiencies and low operational costs due to the high affinity of microorganisms for the target VOCs, and to the reduced energetic needs and the lack of chemical reagents, respectively (Estrada et al., 2011). Interestingly, Van Groenestijn & Kraakman (2005) estimated that in 2005 there were probably over 7500 biological waste gas treatment systems and related systems installed in Europe, of which half were installed at sewage treatment and composting plants. Besides, off-gas treatment biotechnologies are environmentally friendly since they transform pollutants into innocuous by-products such as water, CO_2 or new cellular matter. Nowadays, the use of bioreactors for gaseous effluents is a recognised technology that has been successfully applied in a wide range of industries for the abatement of a large variety of organic and inorganic pollutants, odorous emissions and it is also showing its relevance in the case of the main GHGs such as methane and nitrous oxide (Utami et al., 2011; Avalos Ramirez et al., 2012).

In these bioreactors, oxygen and pollutants are transferred from the gas to the aqueous phase, and then to the biofilm, where the pollutants are oxidized by microorganisms (mainly bacteria and fungi). Thus, the degradation rate in bioreactors will be determined by a serial mechanism comprised of pollutant mass transfer from the gas phase, diffusion within the biofilm and its subsequent biodegradation (see Figure 1). Some studies have shown that the presence of the biofilm enhances the mass transfer of the hydrophobic substances due to the hydrophobic nature of biofilms, especially if fungi are present within the microbial community (Revah & Morgan-Sagastume, 2005).

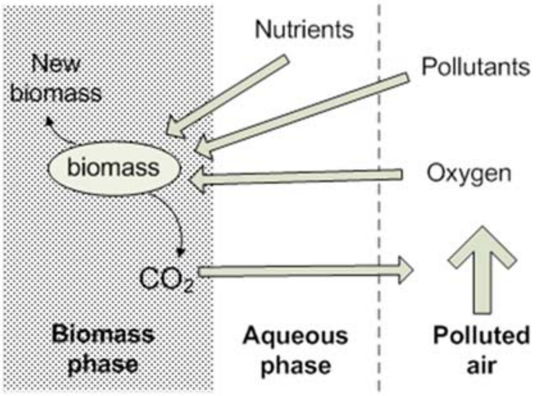

Figure 1. *Odorant biodegradation mechanisms in bioreactors*

There is a wide variety of organic and inorganic pollutants that can be treated in bioreactors. The pollutant or the mixture has to be partially biodegradable, soluble in water and should not have any toxic effects on the microorganisms. In general, low molecular weight organic compounds, with high water solubilities and simple bonds can be successfully treated in bioreactors (Devinny et al., 1999). Among the most easily biodegradable substances are alcohols, aldehydes and ketones. Other typical inorganic compounds such as H_2S and NH_3 can be easily biodegraded. Instead, hydrophobic substances with high molecular weights and/or pollutants with complex bonds will present lower biodegradation rates.

The composition of the degrading microbial community depends on the characteristics of the contaminant to be treated. Biotechnologies are suitable for elimination of biodegradable compounds from low to moderate concentrations (1 to 5000 ppm_v). Most microorganisms present in the inoculum (usually activated sludge) are capable of using alcohols, ketones, ethers, etc. as carbon and energy source. However, recalcitrant VOCs (such as halogenated hydrocarbons) will require specialized microorganisms (Delhoménie & Heitz, 2005).

Since the efficiency of these biological processes is very dependent on the metabolic activity of the microbial community, parameters such as temperature, pH, water content, nutrients availability (nitrogen, phosphorus, sulphur, etc.) among others must be carefully controlled to ensure a reliable and efficient operation. Research on the influence of these parameters on the overall process performance have contributed to improve the understanding of biotechnologies in terms of design and control (Lee et al., 2000; Muñoz et al., 2007).

Bioreactors can be classified in different categories depending on the type of the mobile and stationary phases. The concepts of bioscrubbers and activated sludge diffusion systems are used if microorganisms are suspended in the aqueous phase. On the contrary, biofilters and biotrickling filters refer to the attachment of the microbial population on a fixed support.

Biofilters

In biofilters (Figure 2), the waste gas is usually passed through a humidification step prior to its feeding through a packed bed with an organic packing material such as compost, wood or bark chips, peat, etc., or a mixture of some of them. Microorganisms develop as a biofilm onto this support, which can also provide extra nutrients to support bacterial growth. This is quite advantageous since it theoretically eliminates the need for the continuous supply of a liquid stream containing extra nutrients. However, in order to ensure a proper water content inside the packed bed, as well as to favour the wash-out of degradation by-products, discontinuous sprinkling of water over the filter bed is applied. Too low water contents can inhibit biological activity, but a too high humidification can lead to the increase of mass transfer resistance, possible generation of anaerobic zones and even to packing flooding.

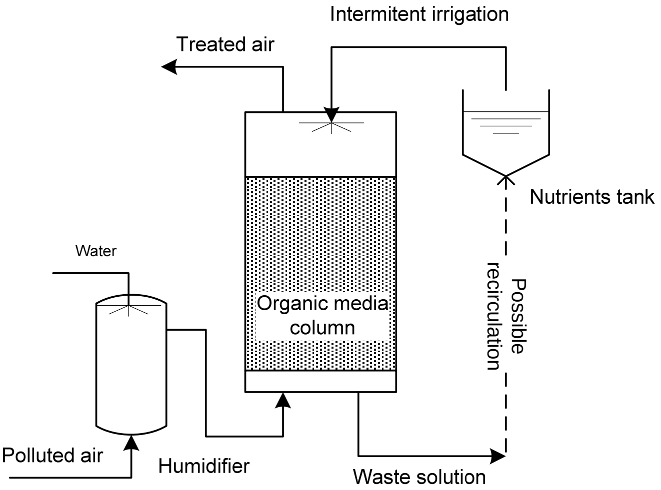

Figure 2. *Schematic design of a biofilter*

A recent study performed by Iranpour et al. (2005) in WWTP employing biofilters for odour treatment showed odour reduction efficiencies always greater than 80%. However, although 90-100% removal efficiencies for H_2S were easily achieved, lower performances were often observed for sulphur compounds (20-100%) or VOCs. Moreover, VOC removal efficiencies are generally below 90% (sometimes as low as 20%, although usually with a wide range of variations), even for easily biodegradable VOCs such as acetone and toluene, which indicates that operational parameters such as water content, temperature, pH, inorganic salts accumulation, etc. should be adequately controlled to ensure a reliable and efficient operation.

Biotrickling filters

The main specific difference of biotrickling filters when compared with biofilters is the presence of a continuous recycling liquid phase as well as the use of a synthetic packing material, chemically inert (Figure 3). Typical support materials employed are plastics, resins, ceramics, rocks, granular activated carbon, etc. Due to the inert nature of the packing material, biotrickling filters need to be inoculated and require the periodical addition of a liquid nutrient solution in order to maintain microbial activity. The polluted gas is fed co- or countercurrently to the liquid flow. The presence of the liquid phase allows the control of the biological process through monitoring of operational factors such as pH control, nutrients content, by-products wash-out, etc.

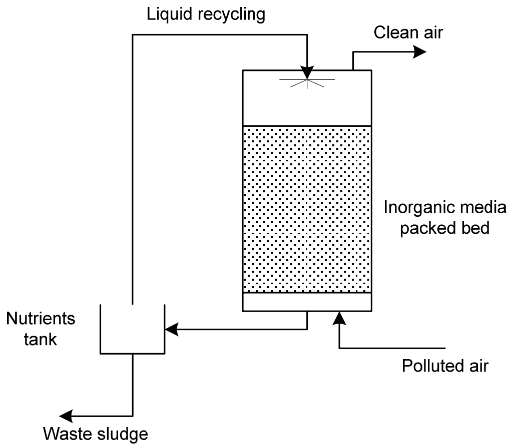

***Figure 3**. Schematic design of a biotrickling filter*

Due to the presence of a continuously recycling liquid phase, biotrickling filters are not appropriate for poorly water-soluble pollutants, but very good for readily soluble ones. Therefore, this configuration is especially suitable for the treatment of hydrophilic compounds with Henry constants lower than 0.1. Typically, biotrickling filters operate at gas residence times from 1 to 15 s and are packed with inert supports exhibiting a low porosity and high specific surface areas (between 100 and 400 m^2m^{-3}) to avoid high pressure drops (often ranging from 100-400 Pa m_{bed}^{-1}) and filter clogging (Revah & Morgan-Sagastume 2005). The lifetime of most conventional packing materials range from 8 to 10 years. Biotrickling filters have shown excellent results in WWTPs achieving H_2S removal efficiencies of 100% at gas residence times comparable to those of physicochemical techniques (between 1.6 and 2.2 s). However, biofilters are still the most employed configuration due to their successful performance treating VOCs.

Bioscrubbers

This process takes place in two separate but interconnected units: an absorption tower where pollutants are transferred from the contaminated gas stream to a recirculating aqueous phase, and a suspended biomass growth bioreactor where biodegradation occurs. The final liquid effluent from the biological unit (after biomass separation) is recirculated to the absorption tower whereas a certain fraction is purged and renewed (Fig. 4).

Absorption tower packing materials, usually inert, must favour mass transfer from the air to the aqueous phase. Since the system completely relies on an initial absorber unit, only highly water-soluble pollutants can be efficiently treated (Herrygers et al., 2004). However, it allows for a precise control of the liquid phase composition by nutrients supply and by-product purge, since they are mainly produced inside the stirred reactor where no clogging problems can occur. Operating parameters, such as pH or temperature are also easily controlled in this particular biotechnology (Burgess et al., 2001).

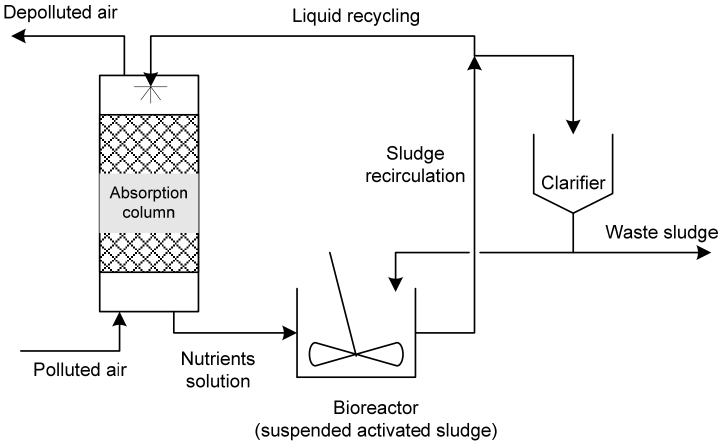

Figure 4. *Schematic design of a bioscrubber*

As aforementioned, bioscrubbers are mainly used for treating contaminants with Henry law constants lower than 0.01, otherwise, gas transfer problems can arise due to the short residence times of the gas in the column. This limitation makes bioscrubbing a less popular biotechnique, since a large part of the VOCs present in WWTPs emissions are moderately hydrophobic.

Activated sludge diffusion bioreactors

Activated sludge diffusion is one of the most promising biotechnologies for waste gas control and an interesting example of suspended-growth systems. The contaminated air is collected from the source and transferred to the activated sludge tank diffusers, which limits its application to WWTPs (Figure 5). The system must be designed to optimize odorant mass transfer from the air bubble to the liquid phase. Once the odorants have diffused into the aqueous phase, they are absorbed by the microbial flocs and biodegraded. Corrosion in pipes, compressors, filters and general equipment due to high H_2S concentrations can be avoided by using adequate corrosion resistant materials (PVC, fibreglass or stainless steel) and moisture traps (Burgess et al., 2001). Recently, Lebrero et al. (2011) confirmed the potential of AS systems as a robust and efficient biotechnology for odour treatment in WWTPs. It is important to note that activated sludge diffusion is especially advantageous for WWTPs using diffused aerated systems due to the low footprint of this technology and to the negligible operating cost, since they can be included in the general costs involved in wastewater treatment.

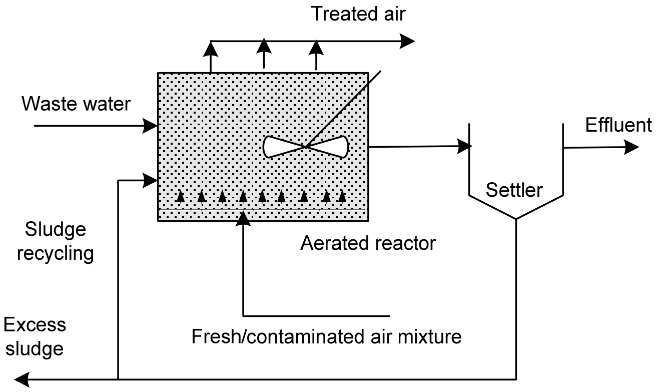

Figure 5. *Schematic design of an activated sludge system*

THE CHALLENGE OF HYDROPHOBIC POLLUTANTS: METHANE

Dilute CH_4 emissions are typically found in some stages of wastewater treatment plants (0-5%), old landfills fugitive emissions (0-20%), in ventilated coal mines (0.1 – 1 %) or in covered liquid manure storage tanks (0-3%). These methane emissions are not suitable for energy recovery, since concentrations lower than 30% have been traditionally treated using flaring or incineration as end of the pipe technologies (Nikiema et al., 2007). However, more than 50% of the anthropogenic CH_4 is emitted at concentrations below 3%, which cannot be treated cost-effectively with oxidation technologies (Avalos-Ramirez et al., 2012). Thus, biological technologies could be an useful tool for the treatment of these emissions, biotrickling filtration being one of the most cost-effective configurations due to its robustness and low operating costs (López et al., 2013).

However, the low solubility of methane into water implies important mass transfer limitations which reduce the abatement potential and hinder the full-scale application of biotrickling filters (BTFs) devoted to the treatment of highly hydrophobic compounds such as CH4 (Kraakman et al., 2011). Most recent research studies have focused on CH4 mass transfer enhancement by either applying complex bioreactor configurations or by adding non-aqueous phases and surfactants to conventional bioreactor configurations (Muñoz et al., 2012). However, both approaches have resulted in limited elimination capacities and entailed high operating costs. Therefore, the development of simple and cost-effective bioreactor configurations and operational strategies devoted to CH4 abatement will be crucial in the global fight against climate change.

So far, studies carried out in biofilters and biotrickling filters treating low methane concentrations (from 0.2 up to 3%) showed the feasibility of the development of methanotrophs at long term to be able to degrade this pollutant in a range from 10 to 50 g $CH4/m^3 \cdot h$. However, these removal capacities do represent still limited removal efficiencies (usually from 10 to 25%). The application of new treatment strategies as well as a deeper knowledge of the process mechanisms involved are both important issues to enhance the effective abatement of highly hydrophobic gaseous pollutants in biological reactors.

CONCLUSIONS

Biotechnologies for polluted gas treatment have been demonstrated as a very convenient strategy both from the point of view of removal efficiencies but also taking into account economic and environmental indicators (Estrada et al., 2012; Alfonsín et al., 2013), especially conventional biofilters and biotrickling filters. Specifically, conventional biofilters, which are usually packed with organic packing materials, are especially suitable for the treatment of relatively poor water soluble compounds. On the contrary, biotrickling filters, in which a liquid phase is supplied in continuously mode, are recommended for the removal of compounds with high solubility. A significant number of studies both at lab, pilot and full-scale have been reported along last decade showing the feasibility of bioreactors for many different gaseous pollutants, even those more hydrophobic, for which new strategies are still under evaluation in order to optimise the process. These technical improvements, together with the need of the development of more cost-efficiency technologies and the increasing awareness of our society about problems related with gaseous emissions (VOCs, odours, GHGs, etc.) show a good perspective to continue with the development and the implementation of these technologies for the abatement of gaseous pollutants in the present and the coming years.

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