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MINI-REVIEW

Biotechnologies for greenhouse gases (CH_4, N_2O, and CO_2) abatement: state of the art and challenges

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Abstract Today, methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) emissions represent approximately 98 % of the total greenhouse gas (GHG) inventory worldwide, and their share is expected to increase significantly in this twenty-first century. CO_2 represents the most important GHG with approximately 77 % of the total GHG emissions (considering its global warming potential) worldwide, while CH_4 and N_2O are emitted to a lesser extent (14 and 8 %, respectively) but exhibit global warming potentials 23 and 298 times higher than that of CO_2, respectively. Most members of the United Nations, based on the urgent need to maintain the global average temperature 2 °C above preindustrial levels, have committed themselves to significantly reduce their GHG emissions. In this context, an active abatement of these emissions will help to achieve these target emission cuts without compromising industrial growth. Nowadays, there are sufficient empirical evidence to support that biological technologies can become, if properly tailored, a low-cost and environmentally friendly alternative to physical/chemical methods for the abatement of GHGs. This study constitutes a state-of-the-art review of the microbiology (biochemistry, kinetics, and waste-to-value processes) and bioreactor technology of CH_4, N_2O, and CO_2 abatement. The potential and limitations of biological GHG degradation processes are critically discussed, and the current knowledge gaps and technology niches in the field are identified.

Keywords Biological treatment · Carbon dioxide · Greenhouse gases · Methane · Nitrous oxide

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Introduction

Today, CH_4, N_2O, and CO_2 emissions represent approximately 98 % of the total greenhouse gas (GHG) inventory worldwide, and their share is expected to increase in this twenty-first century based on their industrial and organic-based nature and the forthcoming scenario of increasing world population (European Environment Agency 2011; Environmental Protection Agency 2011). CH_4, with a global warming potential 23 times higher than that of CO_2 and an atmospheric concentration increasing at 0.2–1 %$year^{-1}$, is mainly emitted from organic waste treatment activities such as landfilling, composting, and wastewater treatment (95 million tons CO_2 equivalent in the European Union [EU]) and livestock farming (166 million tons CO_2 equivalent in the EU) (European Environment Agency 2011). CH_4 represents approximately 14 % of the total GHG emissions worldwide (Intergovernmental Panel on Climate Change 2007). Emissions from compost piles or animal houses typically contain 0–200 mg $CH_4 m^{-3}$, while these concentrations can increase up to 20–100 g $CH_4 m^{-3}$ in old landfills (Nikiema et al. 2007). On the other hand, N_2O is not only a major GHG with a global warming potential 298 times higher than that of CO_2 but it is also the most important O_3-depleting substance emitted in the twenty-first century, with yearly atmospheric concentration increases of 0.3 % (Ravishankara et al. 2009). In the EU-27, N_2O is mainly emitted in waste treatment activities (10 million tons CO_2 equivalent), nitric and adipic acid production (27 million tons CO_2 equivalent), and livestock farming (21 million tons CO_2 equivalent) (European Environment Agency 2011). N_2O contributes to 8 % of the GHG emissions worldwide (Intergovernmental Panel on Climate Change 2007). Concentrations ranging from 10 to 2,000 mg $N_2O m^{-3}$ are common in the emissions of these activities (Xu et al. 2004; Kampschreur et al. 2008). Even in tanks with novel

microbial nitrogen removal processes such as nitritation/anaerobic ammonium oxidation (anammox), significant amounts of N_2O have been recorded during wastewater treatment (Kampschreur et al. 2008). Finally, CO_2 represents the most important GHG with approximately 77 % of the total GHG emissions worldwide and an annual atmospheric concentration increase of 0.5 % over the last decade (Intergovernmental Panel on Climate Change 2007). CO_2 is mainly produced in electricity and heat production processes (1,400 million tons), transport (960 million tons), industrial and fuel manufacturing (700 million tons), and other sectors (e.g., commercial, residential, or agricultural; with 670 million tons). Typical CO_2 concentrations in combustion gases range from approximately 90 to 270 $g\,m^{-3}$ (European Environment Agency 2011).

Most members of the United Nations, based on the urgent need to maintain the global average temperature 2 °C above preindustrial levels, have committed themselves to significantly reduce their GHG emissions (Intergovernmental Panel on Climate Change 2007). In this context, an active abatement of these emissions will help to achieve these target emission cuts without compromising industrial growth. Besides, the development of cost-efficient GHG abatement methods might be of paramount importance in the near future since recent monitoring campaigns in waste treatment facilities, for instance, have shown that the CH_4 and N_2O emissions reported might be underestimated by one order of magnitude (Foley et al. 2010; Ahn et al. 2010). As a matter of fact, most international GHG inventories have based their estimations on Intergovernmental Panel on Climate Change emission factors, and there is increasing evidence that some of these factors, for instance, those applied to waste treatment activities, might lack a scientific basis or be based on studies under very specific and non-extrapolable conditions (Foley et al. 2010; Ahn et al. 2010). In addition, the gradual application of the EU Landfill Directive 1999/31 (enforcing a reduction in the organic matter content of the solid waste to be disposed) will result in emissions with lower CH_4 concentrations, which will significantly limit the implementation of conventional energy recovery-based treatment technologies and will require the application of cost-efficient abatement methods for diluted CH_4 streams.

However, despite the environmental relevance of CH_4, N_2O, and CO_2 emissions, the development of cost-efficient and environmentally friendly GHG treatment technologies (especially of those intended for the treatment of emissions containing low GHG concentrations) has been scarce. Today, physical/chemical treatment methods for CH_4 abatement such as activated carbon adsorption or incineration are either inefficient or costly at the low concentrations typically found in emissions from waste treatment and animal farming and possess a high CO_2 footprint as a result of their intensive energy usage (Melse and Van der Werf 2005). On the other hand, conventional NO_x treatment technologies such as selective catalytic reduction or selective noncatalytic reduction present prohibitive operating costs (and large environmental impacts) when treating large air flow rates containing low concentrations of NO_x as a result of their intensive energy use (Skalska et al. 2010). Similarly, CO_2 sequestration through physical/chemical methods, such as gas scrubbing with alkaline or amine solutions or direct injection into subsurface natural reservoirs (storage), entails prohibitive costs and secondary environmental pollution (Herzog 2001; Kumar et al. 2011). In this regard, biotechnologies can become, if properly tailored, a low-cost and environmentally friendly alternative to physical/chemical methods for the abatement of CH_4, N_2O, and CO_2. Biotechnologies, which are based on the biocatalytic action of specialized bacteria, microalgae, or fungi, have been consistently proven as robust and efficient abatement methods for the treatment of industrial volatile organic compounds and malodors, exhibiting lower operating costs and environmental impacts than their physical/chemical counterparts (Estrada et al. 2011, 2012b). This study constitutes a state-of-the-art review of the microbiology (biochemistry, kinetics, and waste-to-value processes) and bioreactor technology of CH_4, N_2O, and CO_2 abatement. The potential and limitations of biological GHG degradation processes are critically discussed, and the current knowledge gaps and technological research niches in the field are identified.

Biological CH_4 removal

Microbiology of CH_4 removal

Methanotrophs are methylotrophic bacteria able to utilize CH_4 as the sole carbon and energy source, although several yeast genera such as *Sporobolomyces* and *Rhodotorula* or even the green microalgae *Chlorella* have been reported as methane oxidizers (Enebo 1967; Wolf and Hanson 1979). Most methanotrophs oxidize CH_4 in the presence of O_2, although some strains can couple the oxidation of CH_4 to the reduction of sulfate, nitrate, nitrite, manganese, or iron (Beal et al. 2009; Knittel and Boetius 2009; Ettwig et al. 2010). Methanotrophs are ubiquitous in the environment and commonly found in tundra and wetlands, freshwater and eutrophic lakes, marine sediments and water columns, sewage sludge, rice paddies, agricultural soils and peat bogs, preferentially in the interface between aerobic and anaerobic areas with substantial fluxes of CH_4 (Bowman 2006; Hanson and Hanson 1996). Three types of methanotrophs are distinguished: type I methanotrophs are characterized by uniform intracytoplasmic membranes throughout the cell as bundles of vesicular disks, membrane fatty acids with 14–16

carbons, and the use of the ribulose monophosphate pathway (RuMP) for formaldehyde assimilation. These methanotrophs belong to the *Gammaproteobacteria* class and include genera such as *Methylomonas*, *Methylobacter*, *Methylomicrobium*, and *Methylococcus* (Bratina et al. 1992). Encapsulated bacteria of the *Clonothrix* and *Crenothrix* genera within the *Methylococcaceae* family have been also recently identified as type I methanotrophs (Op den Camp et al. 2009). Type II methanotrophs are found within the *Alphaproteobacteria* class (*Methylosinus* and *Methylocystis* genera) and are characterized by intracytoplasmic membranes along the peripheral part of the cell, fatty acids with 18 carbons, and the use of the serine pathway for formaldehyde assimilation (Patt and Hanson 1978; Scott et al. 1981; Hanson and Hanson 1996). Type X methanotrophs contain membrane fatty acids with 16 carbons, use the RuMP pathway, posses a ribulose-1,5-bisphosphate carboxylase, grow at higher temperatures than types I and II, and belong mainly to the *Methylococcus* genera (Davies and Whittenbury 1970; Hanson and Hanson 1996). Despite the fact that most methanotrophs are included in the *Gammaproteobacteria* and *Alphaproteobacteria* classes, some of them belong to the *NC10* phylum (nitrite-respiring methanotrophs), *Verrucomicrobia*, and *Euryarchaeota* (Hanson and Hanson 1996; Hou et al. 2008; Op den Camp et al. 2009; Ettwig et al. 2010; Semrau 2011).

All methanotrophs use methane monooxygenases (MMOs) during the aerobic oxidation of CH_4 to methanol, utilizing reducing equivalents for the split of the O_2 bonds. Two forms of MMOs have been identified in methanotrophs: soluble and particulate. The soluble MMO form (sMMO) was first detected in the cytosol of methanotrophs II and X and recently identified in type I (Koh et al. 1993; Hanson and Hanson 1996). This monooxygenase has a broader range of substrates than other monooxygenases and it is composed of a hydroxylase, a reductase, and a regulatory protein (Lipscomb 1994; Hanson and Hanson 1996; Wallar and Lipscomb 2001). sMMOs are synthesized when levels of Cu^{2+} are below 0.86 $\mu mol\,g^{-1}$ dry weight (dw) and contain iron as an important cofactor in the reaction center (Hanson and Hanson 1996; Nielsen et al. 1997; Choi et al. 2003). On the other hand, particulate or membrane-bound MMOs (pMMO) are constitutive in all aerobic methanotrophs at Cu^{2+} concentrations above 0.86 $\mu mol\,g^{-1}$ dw, except in the genera *Methyloferula* and *Methylocella* (Dalton 1992; Semrau et al. 2010). pMMO is also composed of three polypeptides, which exhibit a lower specific activity compared to sMMO, but nowadays, little is known about its molecular properties (Basu et al. 2003; Choi et al. 2005). Soluble MMOs employ $NADH+H^+$ as reducing agent to oxidize the CH_4 present in the intracellular medium (which previously diffused from the extracellular aqueous medium) to CH_3OH, while pMMO requires a cytochrome complex to oxidize the CH_4 present in the cytoplasm. Then, the periplasmic enzyme methanol dehydrogenase catalyzes the conversion of methanol to formaldehyde (Fig. 1) (O'Connor 1981; Anthony 1982; Dalton 1992; Hanson and Hanson 1996; Glass and Orphan 2012). Formaldehyde is then either converted to formic acid by formaldehyde dehydrogenase or to biomass through the RuMP pathway in type I and X methanotrophs or through the serine pathway in type II methanotrophs (Hanson and Hanson 1996).

Finally, carbon dioxide is produced from formate in an oxidation step catalyzed by formate dehydrogenase with the production of the reducing equivalents required at the initial steps of CH_4 oxidation (Hanson and Hanson 1996; Chistoserdova 2011; Glass and Orphan 2012). Moreover, type X methanotrophs can assimilate formaldehyde through the RuMP pathway while fixing CO_2 using a ribulose-1,5-bisphosphate carboxylase (Whittenbury 1981). For a more extensive discussion of the biochemistry of aerobic CH_4 oxidation, readers are referred to specialized reviews (Higgins et al. 1981; Hanson and Hanson 1996; Semrau et al. 2010).

In contrast to aerobic CH_4 oxidation, the information available in the literature about anaerobic CH_4 oxidation is scarce. Moreover, anaerobic methane-oxidizing archaea, which are responsible for 7–25 % of the total CH_4 oxidation worldwide, can undertake this process in symbiosis with sulfate-reducing bacteria, using CH_4 as an electron donor to convert sulfate into sulfite (Hanson 1980; Hoehler et al. 1995, Reeburgh 2007). On the other hand, aerobic CH_4-oxidizing bacteria can grow concomitantly with denitrifying bacteria, consuming oxygen and producing electron donors for denitrification (Bédard and Knowles 1989; Thalasso et al. 1997). In addition, a recently discovered denitrifying methanotroph *Methylomirabilis oxyfera*, from the phylum *NC10*, is able to perform intra-aerobic CH_4 oxidation utilizing the oxygen contained in nitric oxide (NO) (Wu et al. 2011).

Microbial CH_4 oxidation is often described by both Monod and Michaelis–Menten models. However, the different experimental setups and models used for the estimation of the kinetic parameters often hinder the direct comparison of the data available in literature (Table 1). The Michaelis–Menten constant (K_M) determines the rate of the overall enzymatic activity and ranges from 31.7×10^{-9} to 2.8×10^{-5} M, the lowest value highlighting the high affinity of some bacterial enzymes for CH_4 oxidation (Scheutz et al. 2009). Similarly, the Monod constant (K_S) defines the affinity of microorganisms for the substrates and, in the particular case of CH_4, ranges typically from 1×10^{-6} to 4.74×10^{-4} M. pMMO-bearing bacteria have been reported to exhibit a higher affinity for CH_4 (lower K_S values) than sMMO-bearing microorganisms (Bédard and Knowles

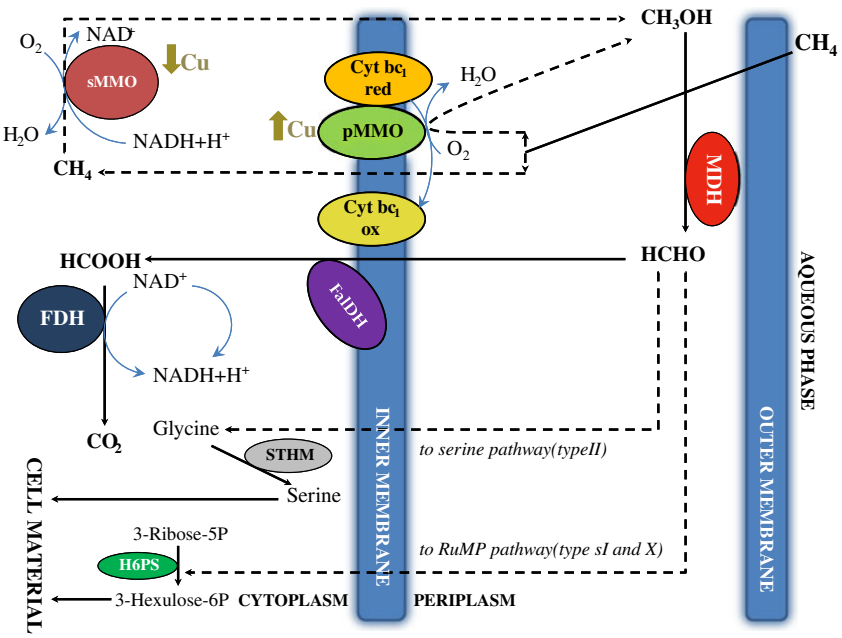

Fig. 1 Methane oxidation pathways in type I and II methanotrophs. *Continuous lines* represent a unidirectional flow in the pathway, while *dashed lines* represent alternative pathways. *sMMO* soluble methane monooxygenase, *pMMO* particulate methane monooxygenase, *MDH* methanol dehydrogenase, *FDH* formate dehydrogenase, *FalDH* formaldehyde dehydrogenase, *cyt red/ox* cytochrome reduced/oxidized, *STHM* serine hydroxymethyltransferase, *H6PS* hexulose-6-phosphate synthase. Adapted from Hanson and Hanson (1996) and Semrau et al. (2010)

1989). Moreover, the maximum CH_4 oxidation rates (V_{max}) are often reported in a wide variety of units, with values ranging from 0.02 to 0.6 $g m^{-3} h^{-1}$, from 1.48×10^{-4} to 25.7 $g m^{-2} h^{-1}$, from 2.88×10^{-6} to 0.50 $g g^{-1} h^{-1}$, and from 3.2×10^{-15} to 1.44×10^{-12} g $cell^{-1} h^{-1}$. Varied biomass yields ranging from 0.02 to 0.8 g biomass g CH_4^{-1} are also typically found in the literature (Arcangeli and Arvin 1999).

The rates of CH_4 oxidation depend on parameters such as dissolved oxygen and CH_4 concentrations, moisture content in the media, temperature, pH, type of nitrogen source, or copper levels. Hence, both types I and II methanotrophs exhibit their maximum oxidation rate at gas oxygen concentrations ranging from 1.5 to 10.5 % *v/v* (Whittenbury and Dalton 1981; Wilshusen et al. 2004). Furthermore, high CH_4/O_2 ratios stimulated the growth of type II methanotrophs (high K_M), while low CH_4/O_2 ratios stimulated the growth of type I methanotrophs (low K_M) (Bender and Conrad 1995; Amaral and Knowles 1995). These findings support the hypothesis that sMMOs are usually expressed at high CH_4 concentrations and pMMO at low CH_4 concentrations (Lontoh and Semrau 1998; Henckel et al. 2000). The optimum moisture content for methanotroph growth was shown to be packing media specific, which will be discussed later on in the reactor section. Methanotrophs are mesophilic microorganisms, although thermotolerant and thermophilic *Methylothermus*, *Methylocaldum*, *Methylococcus*, or *Verrucomicrobia* strains have been isolated from hot springs, with an optimal growth in the range of 42–65 °C (Bodrossy et al. 1999; Tsubota et al. 2005). Psychrophilic strains of *Methylobacter*, *Methylosphaera*, and *Methylomonas* have been isolated from tundra soils, Antarctic meromictic lakes, and deep igneous groundwater, exhibiting an optimal growth range of 3.5–15 °C (Omelchenko et al. 1993; Bowman et al. 1997; Kalyuzhnaya et al. 1999). Hence, maximum oxidation rates in composite soils occurred at 31 °C, while in most peat soils, the optimal temperature was 25 °C (Bédard and Knowles 1989; Whalen et al. 1990; Dunfield et al. 1993; Bender and Conrad 1995). On the other hand, low CH_4 oxidation rates were recorded in samples from forest and landfill cover soils at 2–5 °C (Whalen and Reeburgh 1996; Christophersen et al. 2000). Species from the *Methylocella* and *Methylocapsa* genera or the *Verrucomicrobia* phylum exhibiting an optimum growth at pH 2–2.5 have been isolated from acidic environments, but most methanotrophs preferably live and oxidize CH_4 at pH 7–7.65 (Bender and Conrad 1995; Dedysh et al. 1998, 2002; Pol et al. 2007; Dunfield et al. 2007). Oxidation rates by acidophilic methanotrophs have been found to be higher in samples from acidic peat soils (pH values of 4–5) compared to those from neutral soils (pH values of 6–8) (Born et al. 1990; Dunfield et al. 1993). Despite type II methanotrophs being able to express the enzyme nitrogenase at low O_2 levels and perform N_2 fixation, nitrate and ammonia are the preferred N sources (Quayle 1972). Type I methanotrophs are dominant in environments with low methane concentrations and high inorganic nitrogen levels, while type II methanotrophs are often predominant in scenarios with high CH_4/N ratios (Amaral and Knowles 1995). Microbial stimulation or inhibition mediated by inorganic nitrogen sources such as ammonia or nitrate depend on the nitrogen and CH_4 concentration, the pH, and the type of methanotroph. Hence, optimal growth and CH_4 oxidation rates were recorded at 12–61 mM ammonia for some methanotrophic communities, while some studies revealed that concentrations of 4–10 mM could reduce CH_4

Table 1 Maximum CH_4 oxidation rates and kinetics parameters obtained in different environmental conditions

V_{max}	Conditions	Kinetics	Reference
1.48×10^{-4} g m^{-2} h^{-1}	Samples from aerated and temperate forest soils	–	Born et al. (1990)
1.88 g m^{-2} h^{-1}	Samples from landfill cover soils	K_S=2.5–9.3×10^{-6}M, Y_x=0.19–0.69 g biomass g^{-1} CH_4	Whalen et al. (1990)
6.93 g m^{-2} h^{-1}	Samples from microcosms	K_M=31.7×10^{-9}M	Kightley et al. (1995)
25.7 g m^{-2} h^{-1}	Samples from deep in landfill soils	–	Börjesson et al. (1998)
10.08 g m^{-2} h^{-1}	Biocovers with compost and polyestyrene pellets	–	Powelson et al. (2006)
2.88×10^{-6} g g^{-1} h^{-1}	Yeasts with slow generation times ranging 2–7 days	–	Wolf and Hanson (1979)
0.50 g g^{-1} h^{-1}	Pure cultures	K_M=1 or 3×10^{-6}M for pMMO/sMMO, respectively	Bédard and Knowles (1989)
5.9×10^{-5} g g^{-1} h^{-1}	Preincubated natural oxic soils	K_M=0.17–2.79×10^{-5}M	Bender and Conrad (1992)
1.28×10^{-4} g g^{-1} h^{-1}	Landfill cover soils with compost	–	Figueroa (1993)
0.08 g g^{-1} h^{-1}	Soils enriched with CH_4 and O_2	–	Brusseau et al. (1994)
1.73×10^{-4} g g^{-1} h^{-1}	Samples of silty loam	–	Börjesson (1997)
0.1 g g^{-1} h^{-1}	*M. organophilum* CZ-2 in reactors with nitrogen limitation	–	Zúñiga et al. (2011)
4.16×10^{-5} g g^{-1} h^{-1}	Samples from a biofilter integrated into a landfill cover system; low affinity methane oxidizers	K_M=15.1×10^{-6}M	Gebert et al. (2003)
3.2×10^{-15} g×cell^{-1}×h^{-1}	*M. trichosporium*	–	Knowles (1993)
1.44×10^{-12} g×cell^{-1}×h^{-1}	Samples from freshwater sediments	–	Bender and Conrad (1994)
3.2×10^{-14} g×cell^{-1}×h^{-1}	Concentration range of 10–100 ppm_v	–	Knief and Dunfield (2005)
1.12×10^{-2} g m^{-3} h^{-1}	Samples from Lake Superior sediments	K_M=4.6×10^{-6}M	Remsen et al. (1989)
0.20–0.56 g m^{-3} h^{-1}	Sediment pore water samples from Lake Michigan	K_S=4.38–9.38×10^{-6}M	Buchholz et al. (1995)
0.17 g m^{-3} h^{-1}	Concentrations of 3,000 ppm_v; *M. trichosporium* OB3b	–	Yoon et al. (2010)
0.06 g m^{-3} h^{-1}	Sandy sediments in Brian seep with low CH_4 dissolved	–	Treude and Ziebis (2010)
0.15 g m^{-3} h^{-1}	Seep sediments from Coal Oil Point with a majority of *Methylococcus* in population	–	Håvelsrud et al. (2011)
–	Pure cultures without diffusion limitation	K_S=1–2×10^{-6}M	Joergensen (1985)
–	14,500–27,000 ppm_v	μ_{max}=0.05 h^{-1}, K_S=4.74×10^{-4}M, Y_x=0.8 g biomass g^{-1} CH_4	Delhoménie et al. (2009)

oxidation by 30 % (Bender and Conrad 1995). Some in situ investigations suggest that high ammonia concentrations could inhibit CH_4 oxidation either by toxicity or enzymatic competition, although such detrimental effects could be also due to a nitrite accumulation from ammonia oxidation (Bédard and Knowles 1989). In this context, ammonia fertilizers seem to be more hazardous to type II than to type I methanotrophs (Mohanty et al. 2006). Copper positively regulates the activity of pMMO/sMMO and controls the expression of their genes (Stanley et al. 1983; Dalton et al. 1984). However, Cu^{2+} concentrations have to be controlled in order to maintain copper homeostasis and prevent metal toxicity. The optimal growth of most methanotrophs is achieved at cooper concentrations lower than 4.3 mM (Bender and Conrad 1995), although a combination of high Cu levels and organic material can favor the rapid growth of type II methanotrophs (Graham et al. 1993). Besides, in Cu-limiting scenarios, some aerobic methanotrophs excrete a molecule called methanobactin able to bind cooper in the extracellular medium and actively transport it into the cell at concentrations as low as 0.7–1 μM (Kim et al. 2004; Balasubramanian et al. 2011).

Microbial CH_4 oxidation can be coupled with the production of high added-value biotechnological products. Thus, some methanotrophs can utilize acetyl-CoA from the serine or RuMP pathways to form polyhydroxyalkanoates such as polyhydroxybutyrate (PHB), an important commodity in the bioplastic industry (Higgins et al. 1981; Lidstrom and Stirling 1990). PHB generation can be stimulated under N-, S-, or Mg-limiting conditions. For instance, N limitations supported the production of PHB at 39 % (*w*/*w*) in *Methylobacterium organophilum* in a bioreactor and even at

57 % (*w*/*w*) in serological glass bottles (Zúñiga et al. 2011). Exopolysaccharides at 62 % (*w*/*w*) can be also produced from CH_4 oxidation using *Methylocystis parvus* (Hou et al. 1978; Chida et al. 1983). CH_4-oxidizing bacteria, as well as algae, fungi, or yeasts, can be also used in single-cell protein production for human and animal consumption. For instance, Norferm Danmark A/S in Norway produces 8,000 tons protein$year^{-1}$ (BioProtein) from *Methylococcus capsulatus* Bath (Winder 2004).

Reactors for biological CH_4 oxidation

Several bioreactor configurations such as biofilters, biotrickling filters, airlifts, and stirred tanks have been used for CH_4 abatement from air emissions (Fig. 2). Biotechnologies for CH_4 abatement have been implemented in enclosed bioreactors where the polluted air (containing O_2) is supplied by forced ventilation in either upflow or downflow mode and in open bioreactors where the CH_4-bearing emission (e.g., landfill gas) is supplied upwards at the bottom of the system, while O_2 diffuses from the air at the top of the bioreactor (Gebert et al. 2001; Gebert and Gröngröft 2006)

Enclosed laboratory-scale bioreactors are the most popular CH_4 abatement systems reported in the literature likely due to the fact that operational parameters such as temperature and moisture content can be controlled. On the other hand, open bioreactors constitute the most implemented technology to treat real CH_4 emissions from landfills at full scale. Unfortunately, forced air ventilation to provide the O_2 needed by aerobic methanotrophs is not recommended when treating real landfill CH_4 emissions to avoid explosion risks (CH_4 concentration in landfill gas in the range of 30–70 % *v*/*v*) (Kallistova et al. 2005; Zamorano et al. 2007). Therefore, O_2 supply in open passively vented biofilters strongly depends on climate conditions, and O_2-limiting conditions are often encountered in these bioreactors (Humer and Lechner 1999; Gebert et al. 2001; Berger et al. 2005). In this regard, a three-dimensional numerical model has been recently developed, incorporating the effect of advection–diffusion gas flows, heat, and moisture on CH_4 oxidation in open biofilters (Hettiarachchi et al. 2011). This innovative model allowed for the estimation of CH_4 removal under several environmental conditions confirming that CH_4 oxidation in open biofilters strongly depends on environmental factors.

Biofilters are by far the most common bioreactors used for CH_4 removal although innovative multiphase systems operated in different bioreactor configurations have emerged in the last 5 years. Despite being relatively simple systems, biofilters constitute the most studied and implemented technology to date and can support high CH_4 removal rates when parameters such as the O_2 concentration or the moisture content are optimized. For instance, biofilter operation in landfills at O_2 concentrations of 18–28 μM (1.7–2.6 % in the gas phase) resulted in maximum oxidation rates of 1.78×10^{-6}mol $CH_4 g^{-1}$ $dw h^{-1}$ (Gebert et al. 2003). The optimum moisture content was shown to depend on water activity, which itself is often packing media specific, with maximum CH_4 oxidation rates at a moisture content of 11 % (*w*/*w*) in composite soils, 10–20 % in landfill cover soils, and 20–35 % in other types of soils, while moisture contents of 5, 56, or 71 % in composite soils supported low oxidations rates (Whalen et al. 1990; Bender and Conrad 1995). The intensive research conducted on biofiltration over the last 20 years has resulted in important advances in packing material technology, evolving from a bed of

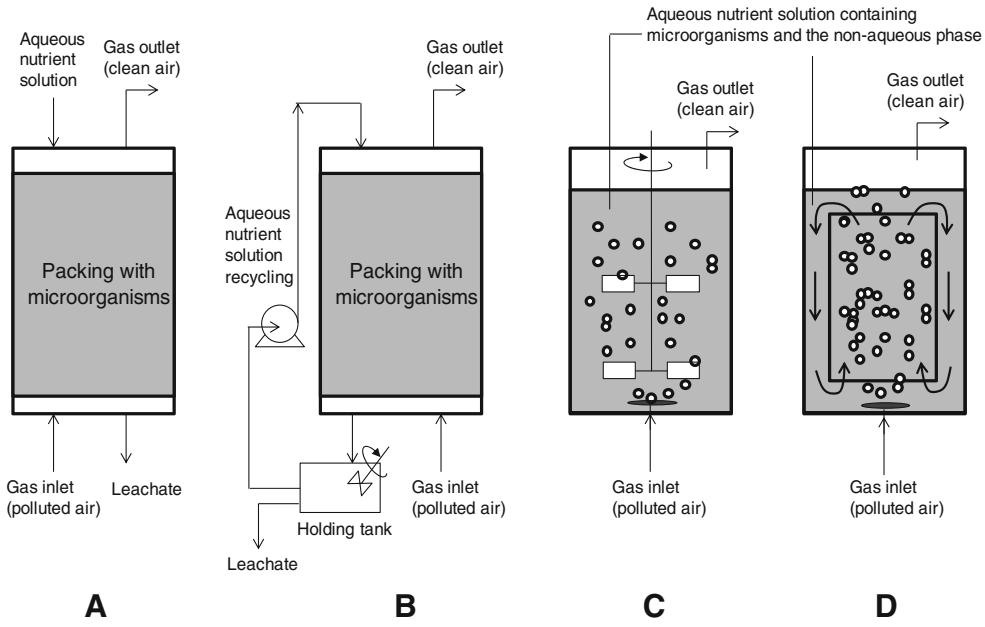

Fig. 2 Bioreactor configurations reported in the literature for CH_4 abatement: **a** biofilter, **b** biotrickling filter, **c** stirred tank, and **d** concentric tube airlift

simple materials such as compost, pine bark, or perlite to more sophisticated structured packings such as metallic or polymeric ring and foams or custom-made nutrients containing polymeric pellets. Besides, optimum environmental conditions, nutrient requirements, and potential inhibitors of CH_4 oxidation in biofilters have been recently identified (Veillette et al. 2012). These breakthroughs in biofiltration technology have resulted in significant reductions in the EBRTs required to efficiently abate CH_4 emissions. For instance, ECs of 1.2–25 $gm^{-3}h^{-1}$ have been recorded in conventional biofilters operated at EBRTs of 10–360 h (Table 2) (du Plessis et al. 2003; Berger et al. 2005; Melse and Van der Werf 2005), while third generation enclosed biofilters operated at EBRTs of 0.3–20 h were able to reach ECs of 65–280 $gm^{-3}h^{-1}$ (Gebert and Gröngröft 2006; Nikiema and Heitz 2009; Park et al. 2009). To the best of our knowledge, Park et al. (2009) reported the highest abatement performance in a biofilter treating CH_4 with a maximum EC of 280 $gm^{-3}h^{-1}$ (corresponding to an RE of 50 %) at an EBRT of 1.2 h. Girard et al. (2011) achieved an EC of 14.5 $gm^{-3}h^{-1}$ in a biofilter operated at an EBRT of 0.07 h. Interestingly, a similar EC to that obtained by Park et al. (2009) would be expected if the ECs obtained by Girard et al. (2011) were multiplied by 17, which is the EBRT ratio between these reports.

Several bioreactor configurations and operation modes have been recently investigated in order to overcome the typical mass transfer limitations encountered in conventional biofilters as a result of the low water solubility of this GHG (Fig. 2). Rocha-Rios et al. (2009, 2011) studied the performance of the so-called two-phase partitioning bioreactors (TPPBs) for CH_4 abatement, which are based on the addition of a nonaqueous phase (e.g., a liquid solvent or a solid polymer) with a high affinity for CH_4, resulting in higher CH_4 absorptions and driving forces for mass transfer (Quijano et al. 2009). Silicone oil, exhibiting 15 times higher affinity for CH_4 than water is one of the most commonly used nonaqueous phases in TPPBs. In this context, a silicone oil-based TPPB implemented in a stirred tank reached a maximum EC of 106 $gm^{-3}h^{-1}$ at an EBRT as short as 0.08 h (corresponding to 4.8 min) (Rocha-Rios et al. 2009). This important reduction in the EBRT dramatically decreased the size of the abatement unit and consequently the overall technology cost. In the quest for less energy-demanding systems than stirred tank reactors, TPPBs have been also implemented in airlift systems with a maximum EC of 22 $gm^{-3}h^{-1}$ at an EBRT of 0.12 h. Nevertheless, a better performance was reported in a TPPB operated as a biotrickling filter, exhibiting a maximum EC of 51 $gm^{-3}h^{-1}$ at an EBRT of 0.08 h (Rocha-Rios et al. 2009). Likewise, Avalos et al. (2012) recently reported that a biotrickling filter (without the nonaqueous phase) using stones as packing material and provided with a nonionic surfactant was able to reach a maximum EC of 21 $gm^{-3}h^{-1}$ at EBRTs as short as 0.07 h (corresponding to 4.2 min). Although promising results have been obtained in TPPBs and single liquid-phase biotrickling filters, more research is still necessary to boost the overwhelming CH_4 abatement potential of biotechnologies.

At this point, it is important to stress that little attention has been given to the microbiological aspects in bioreactors devoted to CH_4 abatement (Scheutz et al. 2009). In some studies, the bioreactors were operated for months to stimulate the growth of the indigenous methanotrophic microorganisms present in the packing materials, which resulted in either very long start-up periods (du Plessis et al. 2003; Einola et al. 2008) or in a poor CH_4 abatement performance (Berger et al. 2005). A more efficient performance and shorter start-up periods were recorded when the bioreactor was inoculated with methanotrophic biomass from the leachate (or directly with a portion of the packing material) of a CH_4-treating biofilter (Nikiema and Heitz 2009; Avalos et al. 2012). The enrichment of methanotrophs from activated sludge of wastewater treatment plants is also another common strategy to produce acclimated inocula and to reduce process start-up periods (Rocha-Rios et al. 2009). On the other hand, Avalos et al. (2012) found that clogging issues were very different in a biotrickling filter packed with clay spheres, polypropylene spheres, and stones, despite using the same biomass and inoculation protocol, the reactor packed with stones being more susceptible to clogging and presenting stability problems. These recent studies, therefore, confirm that microbiology and reactor/packing material design are important research areas to be pursued due to their key role on bioreactor start-up and abatement performance.

Biological N_2O removal

Microbiology of N_2O removal

To date, research on N_2O emission control has been mainly focused on minimizing and/or preventing N_2O generation and its release to the atmosphere. Once N_2O is formed, removal by in situ consumption might be also promoted before implementing end-of-pipe technologies (Desloover et al. 2012). The mitigation strategies developed to date were based on microbiological studies investigating the influence of process operational conditions on N_2O production rates, especially in wastewater treatment plants and composting facilities (Kampschreur et al. 2009; Rassamee et al. 2011). In this context, the elucidation of the complex mechanisms governing the microbial production and consumption of N_2O is crucial to develop cost-effective end-of-pipe biotechnologies for N_2O abatement.

Table 2 Bioreactor configurations for the treatment of CH_4 emissions

Reactor type	Microorganisms	Characteristics	EBRT (h)	CH_4 load ($gm_{reactor}^{-3}h^{-1}$)	Maximum EC ($gm_{reactor}^{-3}h^{-1}$)	Maximum RE (%)	Reference
Biofilter	Indigenous pine bark microorganisms acclimated to CH_4 oxidation for 3 months. Identified strains: *Flexibacter scanti*, *Pseudomonas fluorescens*, and *Pseudomonas aeruginosa*	Packing: mixture of pine bark (particle size, 3–5 mm) and perlite (particle size, 3–5 mm) 70:30 (*v*/*v*)	0.5–10	0.03–16	13	81	du Plessis et al. (2003)
Biofilter	Activated sludge acclimated to CH_4 oxidation (acclimation time not specified)	Packing: mixture of compost and expanded perlite (particle size, 0.6–7.5 mm) 40:60 (*v*/*v*)	0.17–80	0.07–25	19	76	Melse and Van der Werf (2005)
Biofilter	Indigenous microorganisms from the packing material	Packing in layers (from bottom to top): layer 1: capillary barrier of fine gravel (10 cm) and middle sand (30 cm); layer 2: loamy sand (85 cm); layer 3: mixture of sand and compost (35 cm)	360	1.2	1.14	95	Berger et al. (2005)
Biofilter	Indigenous microorganisms from the packing material	Packing: compost (matured yard waste compost degree V)	1.7–7.5	5–29	27.5	95	Haubrichs and Widmann (2006)
		Packing: wood chips/compost 50:50 (*w*/*w*). Wood chips (root timber) with particle size of 20 mm	2–7.5	5–24	21.6	90	
Biofilter	Mesophilic type II-dominated methanotroph consortium (inoculation protocol not described)	Packing in layers (from bottom to top): layer 1: gravel for water drainage (10–30 cm); layer 2: crushed porous clay (67 cm); layer 3: gravel (1.5 cm); layer 4: sand (1.5 cm); layer 5: humic topsoil (loamy sand, 10 cm) covered with grass vegetation	0.4–20	46.4–80	80	100	Gebert and Gröngröft (2006)
Biofilter	Microorganisms contained in the packing material; 5–12 months stabilization	Packing: mechanically–biologically treated municipal solid waste	4–14	2.5–6.5	5.6	85	Einola et al. (2008)
Biofilter	Inoculum: leachate of a biofilter treating CH_4 6 months minimum	Packing: inorganic gravel (cylindrical pieces) and stone (cylindrical pieces)	0.05–0.3	13–130	65	50	Nikiema and Heitz (2009)
Biofilter	Indigenous microorganisms from the packing material	Packing: cover soil from a municipal solid waste landfill mixed with earthworm cast 60:40 (*w*/*w*)	0.07–1.2	31–560	280	50	Park et al. (2009)
Biofilter	Not specified	Packing: gravel (particle size: 4–8 mm) with a void space of 40 %	0.07	5–28	14.5	52	Girard et al. (2011)
Multiphase stirred tank	Inoculum: methanotrophic consortium from a wastewater treatment plant. The consortium was acclimated to CH_4 oxidation for 1 month	Stirred tank with two Rushton turbines operated at 800 rpm. 10 % (*v*/*v*) silicone oil was used as nonaqueous phase	0.08	187	106	57	Rocha-Rios et al. (2009)
Multiphase biotrickling filter	Inoculum: methanotrophic consortium from a wastewater treatment plant. The consortium was acclimated to CH_4 oxidation for 1 month	Packing: polyurethane foam (porosity, 0.97; specific area, 600 m^2m^{-3}; density, 35 kgm^{-3}). Mineral salt medium recycling rate of $8\times10^{-4}mh^{-1}$; 10 % (*v*/*v*) silicone oil was used as nonaqueous phase	0.08	131	51	39	Rocha-Rios et al. (2009)

Table 2 (continued)

Reactor type	Microorganisms	Characteristics	EBRT (h)	CH_4 load ($gm_{reactor}^{-3} h^{-1}$)	Maximum EC ($gm_{reactor}^{-3} h^{-1}$)	Maximum RE (%)	Reference
Multiphase airlift reactor	Inoculum: methanotrophic consortium from a wastewater treatment plant. The consortium was acclimated to CH_4 oxidation for 1 month	Concentric tube airlift reactor (column-to-concentric tube area ratio, 1.63). Air flow recirculation, 1–2 $m_{air}^3 m_{reactor}^{-3} min^{-1}$; 10 % (v/v) silicone oil or Desmopan were used as nonaqueous phases	0.12	170	22	13	Rocha-Rios et al. (2011)
Biotrickling filter	Inoculum: lixiviate from a biofilter treating CH_4 for more than 1 year	Packing: clay spheres (particle size, 1.2 cm; specific surface, 310 $m^2 m^{-3}$)	0.07	62	10	16	Avalos et al. (2012)
		Packing: polypropylene spheres (particle size, 2.5 cm; specific surface, 280 $m^2 m^{-3}$)	0.07	62	8	13	
		Packing: stones (particle size, 0.73 cm; specific surface, 470 $m^2 m^{-3}$)	0.07	62	21	34	

N_2O may be biologically produced by both nitrification and denitrification processes (Fig. 3). Nitrification is a sequential and predominantly autotrophic process where NH_3 is first oxidized to NO_2^- by ammonia-oxidizing bacteria and then further oxidized to NO_3^- by nitrite-oxidizing bacteria. Conventional denitrification involves NO_3^- reduction by heterotrophic denitrifiers to N_2 through a stepwise reduction sequence involving NO_2^-, NO, and N_2O. Thus, the main routes for N_2O production are hydroxylamine oxidation, nitrifier denitrification, and heterotrophic denitrification (Kampschreur et al. 2009; Desloover et al. 2012; Wunderlin et al. 2012) (Fig. 3).

Hydroxylamine (NH_2OH) is an intermediate in the nitritation step (oxidation of NH_3 to NO_2^-). The oxidation of NH_3 to NH_2OH is catalyzed by an ammonia monooxygenase (Wood 1986; Wrage et al. 2001), while the oxidation of NH_2OH to NO_2^- is catalyzed by a hydroxylamine oxidoreductase (Hooper and Terry 1979). N_2O production occurs via chemical decomposition of NH_2OH in a process called chemodenitrification or through NO_2^- reduction with electron donors such as organic (e.g., amines) or inorganic (e.g., Fe^{2+} and Cu^{2+}) compounds (Wunderlin et al. 2012). During nitrifier denitrification, NH_3 is partially oxidized to NO_2^- and then further reduced to NO, N_2O, and N_2 in a process carried out by a very specific group of microorganisms (Wrage et al. 2001). Since nitrifier denitrification involves both nitritation and denitrification steps, N_2O may thus be produced in both processes (Colliver and Stephenson 2000). Finally, N_2O production during heterotrophic denitrification is caused by an interruption in the last reduction step before reaching the most reduced compound (N_2). Thus, imbalances in the production and consumption of the enzyme nitrous oxide reductase (NOS), which catalyzes N_2O reduction to N_2, have been pointed out as the main responsible of N_2O accumulation (Wunderlin et al. 2012; Glass and Orphan 2012). In brief, suboptimal conditions for nitrification and denitrification are intrinsically related to N_2O emissions. For instance, when nitrification occurs under oxygen-limiting conditions, ammonia-oxidizing bacteria use NO_2^- as the terminal electron acceptor instead of O_2, leading to higher N_2O emissions (Colliver and Stephenson 2000; Wunderlin et al. 2012). Indeed, emissions of N_2O have been also recorded in anammox tanks, although these emissions could not be directly attributed to the anaerobic oxidation of ammonium (Kampschreur et al. 2008). Likewise, the enzyme NOS catalyzing N_2O reduction during heterotrophic denitrification is the most sensitive to O_2, causing incomplete denitrification and N_2O accumulation at high O_2 concentrations (Tallec et al. 2008; Uggetti et al. 2012). High NO_2^- concentrations can also induce an enhanced reduction of this compound to N_2O during nitrification and lower denitrification rates, resulting in an accumulation of NO and N_2O (Kampschreur et al. 2009).

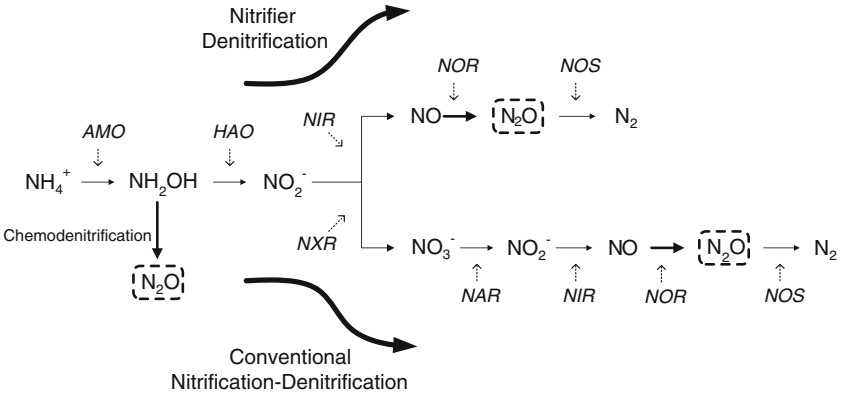

Fig. 3 Overview of the main metabolic routes involved in N_2O production and biodegradation in bacterial cultures. The enzymes responsible of each individual reaction are ammonia monooxygenase (*AMO*), hydroxylamine oxidoreductase (*HAO*), nitrite oxidoreductase (*NXR*), nitrate reductase (*NAR*), nitrite reductase (*NIR*), nitric oxide reductase (*NOR*), and nitrous oxide reductase (*NOS*). Adapted from Wrage et al. (2001), Desloover et al. (2012), and Glass and Orphan (2012)

Based on the fact that the aerobic oxidation of N_2O, to the best of our knowledge, has not been reported yet, any biotechnology devoted to N_2O removal must focus on reducing N_2O to N_2 by favoring the activity of the enzyme (NOS). In this context, the enzyme NOS is known to require Cu in larger quantities than other enzymes, and the reduction of N_2O is thus feasible when Cu is present above a certain threshold concentration (Glass and Orphan 2012). Granger and Ward (2003) observed a low NOS activity in denitrifiers grown at 0.3 nM of total dissolved Cu and a complete consumption of N_2O when Cu was increased up to 10 nM. Environments rich in sulfides might support low N_2O reduction rates since sulfide scavenging and metal precipitation may reduce Cu bioavailability. Very few studies have investigated the potential of microorganisms for N_2O reduction, and the few studies available focused on O_2-free emissions, conditions which are far from those present in most real N_2O emissions. For instance, Apel and Turick (1992) assessed the ability of nine bacterial species to reduce N_2O to N_2 under anaerobic conditions (headspace filled with N_2O and He) in organic synthetic media. Seven species were able to successfully consume N_2O, with *Pseudomonas denitrificans* and *Paracoccus denitrificans* exhibiting the best N_2O biodegradation performance. The optimum temperature for those two species was in the range of 30–35 °C, and maximum N_2O removal rates of 0.017 and 0.015 $mM mg^{-1}$ $dw h^{-1}$ were obtained for *Pseudomonas denitrificans* (initial N_2O concentration of 0.9 mM) and *Paracoccus denitrificans* (initial N_2O concentration of 1.6 mM), respectively. Miyahara et al. (2010) reported that *Pseudomonas stutzeri* TR2 was able to aerobically denitrify with a low production of N_2O, suggesting that bioaugmentation with this strain could reduce N_2O emissions from aerobic wastewater treatment systems due to its improved denitrification ability in the presence of oxygen. *P. stutzeri* TR2 grew at a rate of 0.32 h^{-1}, comparable to the specific growth rates of anaerobic denitrifiers, and was classified by the authors as an expert anaerobic denitrifier.

Bioreactors for N_2O abatement

The implementation of N_2O control strategies is likely to become mandatory in the coming years due to the elevated contribution of this GHG to global warming and ozone depletion. To date, only physical/chemical technologies such as thermal decomposition (Löffler et al. 2002), selective catalytic reduction (Muramatsu et al. 1997; Satsuma et al. 2000), or adsorption (Golden et al. 2004) have been used for the removal of N_2O from off-gases. The application of these abatement methods usually involves the consumption of expensive and/or hazardous chemicals, generation of secondary pollution, and high operating costs when treating high flow rates at the typical low N_2O concentrations. Conversely, biotechnologies offer a more environmentally friendly and cost-effective platform for the removal of N_2O based on their lower energy requirement, absence of hazardous chemicals or catalyst, and innocuous nature of their final end products (N_2 and biomass) (Devinny et al. 1999; Boswell 2001).

Although the number of studies on the application of biological reactors for the removal of N_2O is scarce, their potential has been demonstrated. For instance, Desloover et al. (2011) recently assessed the performance of a bioelectrochemical system with a cation exchange membrane separating the biological anodic and cathodic compartments. In this system, the electrons originated in the anode from sodium acetate biodegradation were supplied to the denitrifying bacteria present in the biocathode and promoted the reduction of N_2O to N_2 according to the equation: $N_2O + 2e^- + 2H^+ \rightarrow N_2 + H_2O$ (E_0=+1.36 V). N_2O removal rates up to 1 $kg_{N2O} Nm^{-3}{}_{\text{net cathodic compartment}} day^{-1}$ were achieved, with a cathodic coulombic efficiency of ≈100 %. However,

although this technology constitutes a promising alternative due to its cost efficiency, challenges regarding its scale-up and sensitivity to aerobic environments still need to be solved (Desloover et al. 2011). Conventional biotechnologies for off-gas treatment such as biofiltration, biotrickling filtration, or bioscrubbing have been rarely applied for N_2O abatement, with most of the studies reported for NO removal based on autotrophic nitrification and heterotrophic denitrification (Shanmugasundram et al. 1993; Nascimento et al. 2000; Chou and Lin 2000; Woertz et al. 2001). For instance, Utami et al. (2012) evaluated the performance of a biofilter packed with a cow manure-based compost batchwise for 9 h at different operating conditions, with the highest N_2O REs (61 %) obtained at an EBRT of 58 min and a moisture content of 50 %. Likewise, Hood (2011) recorded N_2O REs ranging from 14 to 17 % in a biofilter packed with compost and woodchips (30/70 %) at an EBRT of 7.6 s and N_2O inlet concentrations of 0.68–1.24 $mg\,m^{-3}$. Lower N_2O removal efficiencies (0.7 %) were supported by a biofilter packed with pine nuggets and lava rock operated at an EBRT of 5 s, a relative humidity of 90 %, and inlet N_2O concentrations of 428±22.2 ppb_v (Akdeniz et al. 2011). The low performance recorded in these biofilters was probably due to the lack of a specific microbial community acclimated to N_2O biodegradation under aerobic conditions, since these systems were not specifically designed for the abatement of N_2O. Besides, the presence of hydrogen sulfide in some of these air emissions might had promoted the precipitation of metals such as copper, whose presence is mandatory for the synthesis of the enzyme NOS and the correct functioning of N_2O-degrading communities. In brief, the high sensitivity of the biological N_2O reduction step towards the presence of O_2, which is inherent in most N_2O emissions, and the lack of economic or legislative incentive for its removal to date have hindered the development of high performance biological N_2O abatement technologies (Desloover et al. 2012). Nevertheless, the few studies addressing the biological removal of N_2O have shown promising results but require further process optimization.

Biological CO_2 removal

Microbiology of CO_2 removal

Biological CO_2 fixation is carried out via photosynthesis by all terrestrial plants, although microorganisms such as microalgae and cyanobacteria can do it at higher rates and with 10–50 times better efficiency (Costa et al. 2000). Among microalgae, Chlorophyta (including genera such as *Chlamydomonas*, *Chlorella*, *Dunaliella*, *Haematococcus*, *Botryococcus*, or *Scenedesmus*), Euglenophyta (*Euglena*), Bacillariophyta (*Nitzschia*), Rhodophyta (*Porphyridium*), and Eustigmatophyta (*Nannochloropsis*) rank among the most investigated for biological CO_2 fixation (Richmond 2004; Madigan et al. 2006; Barsanti and Gualtieri 2006). Despite constituting a phylum of bacteria rather distant taxonomically, cyanobacteria or blue–green algae are frequently considered as microalgae because of their ability to carry out photosynthesis. Cyanobacteria group includes genera such as *Nostoc*, *Oscillatoria*, *Synechococcus*, *Synechocystis*, *Spirulina*, *Arthrospira*, *Anabaena*, or *Pediastrum*. Both types of photosynthetic microorganisms, from now on referred to as microalgae, are ubiquitous in terrestrial and aquatic environments and can survive in extreme environments such as geysers and hot water springs, desert soils, and Antarctic locations (Madigan et al. 2006; Kumar et al. 2011).

Microalgae use light as the sole source of energy and CO_2 as the sole carbon source during photosynthesis. Nevertheless, some species such as *Chlorella vulgaris*, *Dunaliella salina*, *Euglena gracilis*, and *Tetraselmis tetrathele* also exhibit a concomitant heterotrophic metabolism capable of utilizing from simple organic substrates like acetate, glucose, glutamate, lactate, or amino acids (Gladue and Maxey 1994, Ogbonna and Tanaka 1998) to complex aromatics such as cresols or naphthalene (Semple et al. 1999). Microalgae photosynthesis involves a redox process considered as oxygenic when H_2O acts as the electron donor:

$$CO_2 + H_2O \xrightarrow{\text{light, plant}} (CH_2O)_n + O_2 + \text{Waste heat}$$

At least 8 mol of photons is required to obtain a mole of CH_2O, with 218 KJ $energy\,mol^{-1}$ photons (Ho et al. 2011). CO_2 assimilation during microalgal photosynthesis involves two stages: light reactions where H_2O oxidation to O_2 results in the production of ATP and NADPH and dark reactions where CO_2 is reduced to organic compounds utilizing $NADP^+/NAD^+$ as the electron acceptor.

Light reactions are initiated with light harvesting by the antenna complexes of the thylakoid membranes (Staehelin 1986; Taiz and Zeiger 2002). The excitation energy is then conveyed to the reaction center, where pigments such as chlorophyll *a* absorb a few photons per second with a conversion efficiency of 25–27 % (Taiz and Zeiger 2002). These photons mediate the photolysis of H_2O with the subsequent reduction of chlorophyll P680 from the photosystem II (PSII) (Iverson 2006), the electron transport continuing through quinones, cytochromes, and plastocyanin, finally reaching photosystem I (PSI) and reducing the P700 pigment (Hill and Bendall 1960; Cerveny et al. 2009). Simultaneously, protons are pumped from the thylakoid lumen in order to obtain ATP (Fig. 4).

Dark reactions, also known as Calvin cycle, imply CO_2 fixation and, consequently, the use of the NAD(P)H and

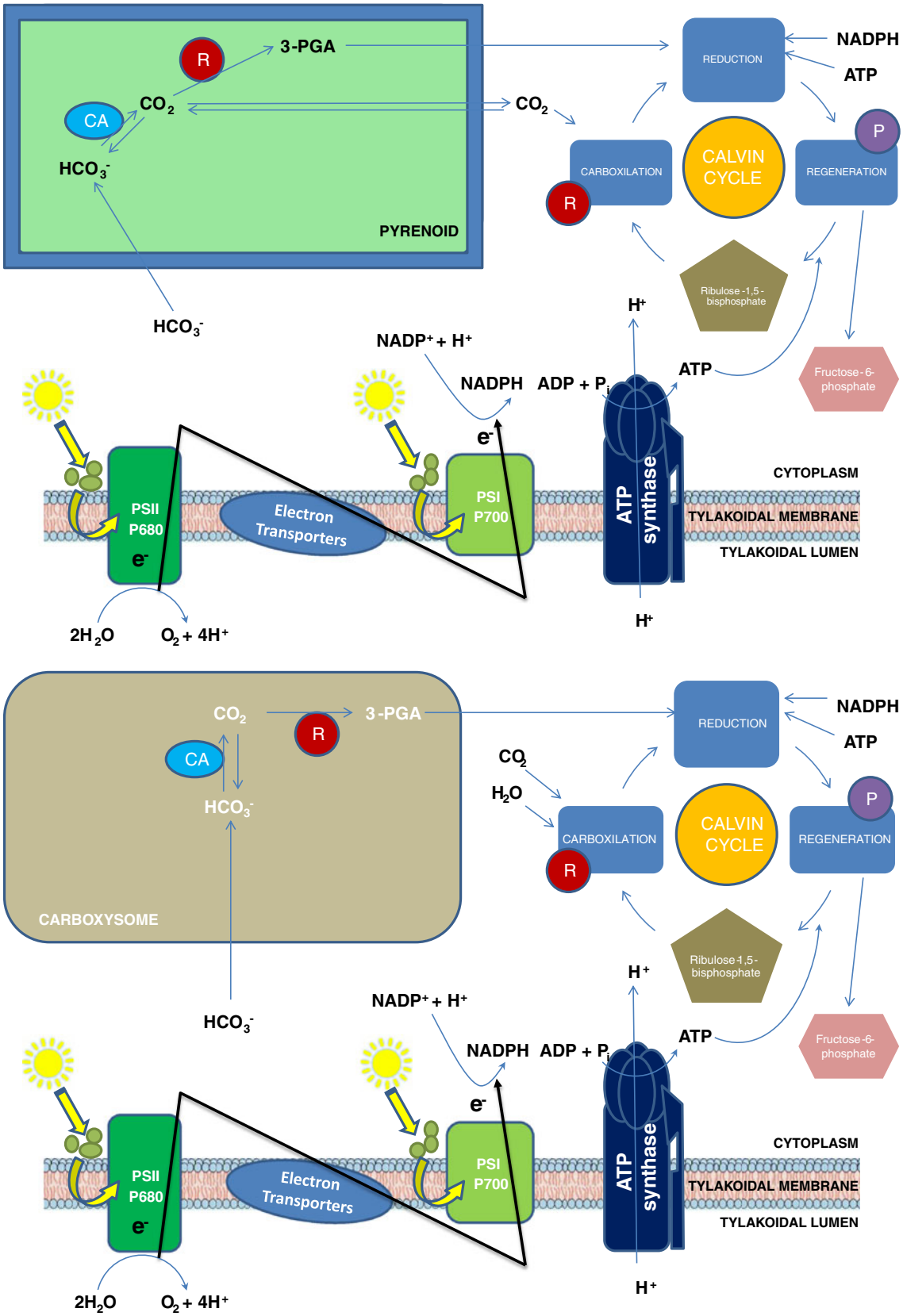

Fig. 4 Carbon and electron fluxes during photosynthesis in green microalgae (*upper figure*) and in cyanobacteria (*lower figure*). The ATP and NADPH produced during the electron transport in the light reactions are used later on for CO_2 reduction in the Calvin cycle. The term "electron transporters" include several components such as quinones, the cytochrome system, or plastocyanin. *R* RuBisCo, *P* phosphoribulokinase, *CA* carbonic anhydrase, *PSII* photosystem II, *PSI* photosystem I

ATP obtained in the light reactions (Calvin 1989; Taiz and Zeiger 2002; Nelson and Cox 2005). The Calvin cycle includes three basic stages: carboxylation of the CO_2 acceptor ribulose-1,5-bisphosphate to 3-phosphoglycerate by the enzyme ribulose bisphosphate carboxylase (RuBisCo), reduction of 3-phosphoglycerate to glyceraldehydes-3-phosphate utilizing the obtained ATP and NADPH, and regeneration of the CO_2 acceptor through a phosphorylation mediated by the enzyme phosphoribulokinase (Fig. 4). Twelve NAD(P)H molecules and 18 ATP molecules are needed to produce a molecule of fructose-6-phosphate from 6 molecules of CO_2 using the RuBisCo (Hall and Rao 1999; Taiz and Zeiger 2002, Madigan et al. 2006):

$$CO_2 + 2NADPH + 3ATP \rightarrow [CH_2O] + 2NADP + 3ADP + 3P_i$$

RuBisCo also exhibits an oxygenase activity and O_2 can compete with CO_2 as substrate, resulting in a process named photorespiration (Miziorko and Lorimer 1983; Edwards and Walker 2004). Photorespiration is favored at high O_2/CO_2 ratios, high temperatures, or high irradiations and can cause a decrease of up to 30–50 % in the photosynthetic efficiency (PE) of microalgae, with the subsequent reduction in CO_2 assimilation (Zhu et al. 2008; Gioardano et al. 2005). The enzyme RuBisCo in microalgae exhibits a low affinity for CO_2, since typical C3 plants present K_M values in the range of 15–25 μM, green algae over 30 μM, and cyanobacteria up to 200 μM (Moroney and Somanchi 1999; Savir et al. 2010). Due to the low affinity of some microalgal species for CO_2, most microalgae and cyanobacteria present specific organelles hosting key enzymes such as RuBisCo and inorganic carbon-concentrating mechanisms (CCMs) (Matsuda et al. 1998; Raven et al. 2008). CCMs consist of ATP-driven plasma membrane pumps induced by low levels of dissolved CO_2. Inorganic carbon-accumulating pumps (CO_2 and HCO_3^-) increase the CO_2 levels in the vicinity of RuBisCo and consequently reduce the extent of photorespiration, even at atmospheric CO_2 levels (0.035 %) (Fig. 4) (Moroney and Somanchi 1999). By using these CCMs, microalgae can concentrate HCO_3^- more than 20-folds over ambient CO_2 levels and cyanobacteria more than 100-folds (Miller et al. 1990). The incorporation of CO_2 into the Calvin cycle requires the conversion of HCO_3^- to CO_2 by a carbonic anhydrase, whose level of expression is also governed by CO_2 concentrations (Price and Badger 1989; Price et al. 1992; Karlsson et al. 1998).

The rates of photosynthetic CO_2 assimilation depend on factors such as the temperature, pH, light intensity, O_2 and CO_2 levels, or presence of inhibitory compounds. Optimal temperatures for microalgae growth and photosynthesis vary from 15 to 25 °C (Tamiya 1957). Despite higher temperatures inducing a reduced photosynthesis due to a decrease in the solubility of CO_2, some microalgae species such as *Chlorella* have been reported to grow optimally in the range of 30–35 °C, which are typically encountered in outdoor cultivations (Pulz 2001). In this context, the isolation of thermophilic species is mandatory in order to implement microalgae-based CO_2 capture methods in power plants, whose exhaust gas emissions are discharged at high temperatures. For instance, *Synechococcus elongatus* was able to fix CO_2 at 60 % *v*/*v* and 52 °C at rates comparable to those recorded at 20 % *v*/*v* and 25 °C (Miyairi 1995). Likewise, thermophilic species of *Chlorogloeopsis* were able to fix CO_2 at 50 °C (Ono and Cuello 2007). Microalgae and cyanobacteria preferentially grow at a neutral pH, although species like *Spirulina platensis* exhibit an optimum pH of 9 and *Chlorococcum littorale* a pH of 4 (Kodama et al. 1993; Hu et al. 1998). The effect of pH on microalgae growth is complex since it is difficult to dissociate the direct effects on microalgae growth from collateral effects such as the modification in the $CO_2/HCO_3^-/CO_3^{2-}$ and NH_3/NH_4^+ equilibria or in phosphorus or heavy metal availability (Muñoz and Guieysse 2006). The photosynthetic activity increases linearly with increasing light intensities up to 400 μmol photon $m^{-2}s^{-1}$, although some species such as *Scenedesmus* or *Chlorella* exhibit saturation thresholds of 100–200 μmol photon $m^{-2}s^{-1}$ (≈5–10 % sunlight) (Hanagata et al. 1992; Muñoz and Guieysse 2006; Tredici 2009). In this context, *S. platensis* was able to withstand light energy fluxes of up to 8,000 μmol photon $m^{-2}s^{-1}$ at a culture density of 8.4±1.6 gL^{-1} under optimum mixing (Hu et al. 1996). Despite the fact that high light intensities can cause photoinhibition over PSII, microalgae strategies such as the reduction in the pigment content, PSII inactivation, or growth under heterotrophic or mixotrophic conditions can minimize its pernicious effects (Behrenfeld et al. 1998; Melis 1999; Ogbonna and Tanaka 2000; Carlsson et al. 2007). Indeed, genetic modifications of microalgae have emerged as a promising tool to reduce the size of the antenna complexes to minimum values of 37 chlorophyll molecules for PSII and 95 for PSI, which can increase photosynthetic efficiencies by 50 % (Nakajima and Ueda 1997; Mitra and Melis 2008; Eriksen 2008). Despite the high solar energy fluxes impinging on the earth surface, microalgae cultivation is often limited by light supply. Hence, considering the sole absorption of the photosynthetically active radiation from the total impinging solar radiation and the energy losses due to reflection, respiration, photosaturation, and photoinhibition, the maximum PE in microalgal culture often decreases from the expected 12.4 % to values of ≈5 % or even lower (Tredici 2009). Microalgae and cyanobacteria are able to efficiently grow at CO_2 atmospheric levels (≈0.0387 % *v*/*v*) but are frequently cultivated at CO_2 levels in the range of 5–15 % *v*/*v* in order to increase microalgal productivities (Kumar et al. 2010a). Microalgae tolerance to CO_2 concentrations is species-dependent with

optimum ranges of 2–15 % *v/v* for *S. platensis* and 15 % for *Nannochloropsis salina* (Doucha et al. 2005; Kumar et al. 2010b). Several strains of the thermophilic red alga *Cyanidium caldarium* were even capable of growing at CO_2 levels of 100 % (Seckbach and Ikan 1972). On the other hand, high dissolved O_2 concentrations (>35 mg L^{-1}) in the cultivation broth favor photorespiration and O_2 radical formation, with the subsequent decrease in microalgal productivity (Pulz 2001; Carvalho et al. 2006; Ho et al. 2011). Finally, heavy metals, NH_3, or industrial gases such as SO_x and NO_x can inhibit microalgae growth. In the context of CO_2 capture from flue gases, NO_x is not as toxic as SO_x towards microalgae and can be even used as nitrogen source. Thus, several *Nannochloropsis* species can grow at 100 ppm_v of NO, while *Dunaliella tertiolecta* can withstand NO_x concentrations of up to 1,000 ppm_v (Yoshihara et al. 1996; Nagase et al. 1998). In contrast, high levels of SO_x (>400 ppm_v) severely reduce the cultivation pH and the photosynthetic rate (Packer 2009; Kumar et al. 2010b). In this regard, *Tetraselmis* species can grow in flue gases containing 14 % *v/v* CO_2, 185 ppm_v of SO_x, and 125 ppm_v of NO_x (Matsumoto et al. 1995).

The ability of *C. vulgaris*, *Botryococcus braunii*, *C. littorale*, *Scenedesmus* sp., *Chlamydomonas reinhardtii*, and *Spirulina* sp. for CO_2 capture was recently assessed based on their high CO_2 fixation rates and ability to yield high added-value products (de Morais and Costa 2007a, b, c; Packer 2009; Ota et al. 2009; Chen et al. 2010; Yoo et al. 2010). Moreover, typical maximum specific growth rates (μ_{max}) of microalgae under photosynthetic, heterotrophic, and mixotrophic conditions are 0.110, 0.098, and 0.198 h^{-1} for *C. vulgaris* and 0.061, 0.040, and 0.048 h^{-1} for *Scenedesmus acutus*, respectively (Ogawa and Aiba 1981).

Microalgae CO_2 capture can also be coupled with the production of high added-value biotechnological products, which would significantly improve the process economy. Thus, health-promoting molecules from *Chlorella* species (Richmond 1990; Gouveia et al. 1996), β-carotenes from *D. salina* (Metting 1996; Ben-Amotz 1999), pharmaceuticals and phycobiliproteins from *S. platensis* (Spolaore et al. 2006; Raja et al. 2008), ketocarotenoid astaxanthins from *Haematococcus pluvialis* (Lee and Ding 1994; Spolaore et al. 2006), carotenes or cosmetics from *Arthrospira* (Richmond 1986; Viskari and Colyer 2003; Spolaore et al. 2006), and eicosapentaenoic acid from *Nannochloropsis* species (Boussiba et al. 1987; Chisti 2007; Chen et al. 2010) rank among the most common high added-value products marketed nowadays and can significantly contribute to the economic viability of microalgae-based CO_2 capture technologies.

Photobioreactors for CO_2 abatement

Photobioreactors (PBRs) are considered "direct" CO_2 capture methods where a CO_2-rich off-gas is directly pumped into the cultivation medium of the bioreactor in contrast to higher plant biomass systems based on CO_2 diffusion (Benemann 1997). The first approach to an engineered microalgae cultivation system dates back to the World War II, when Germany looked for innovative protein sources to replace animal proteins during shortage periods (Carvalho et al. 2006). The concept was further developed during the 1950s and 1960s, but the focus shifted from protein production towards bioenergy production during the first energy crisis in the early 1970s (Chaumont 1993). Today, algal mass cultivation for bioenergy production is still perceived as economically nonsustainable by itself based on the high microalgae production costs (in the range of 4–70€kg^{-1} microalgae depending on the PBR scale) and the relatively low cost of the energy obtained from them (Norsker et al. 2011; Acién et al. 2012a). Hence, the integration of microalgal CO_2 capture with the production of high added-value products or wastewater treatment is nowadays regarded as the only alternative to make the process economically viable (Morweiser et al. 2010; Wang et al. 2008). In this context, recent studies have also shown the possibility of recycling the culture medium after biomass harvesting and a suitable sterilization in the mass production of microalgae to minimize nutrient losses (González López et al. 2013).

The most important parameters in PBR design and operation are light distribution and CO_2 supply, the latter becoming even more relevant when the main goal of the system is CO_2 capture (Morweiser et al. 2010). Scale-up of PBRs is particularly difficult due to the self-shading of cells, which causes the nonhomogeneous distribution of light, and increased mixing rates are sometimes not applicable due to the sensitivity of some photosynthetic strains to shear stress (García Camacho et al. 2011). Apart from the parameters mentioned in the "Microbiology of CO_2 removal" section, the control of sterile conditions, mixing, and removal of O_2 (by high turbulence or stripping with inert gases) is also of paramount relevance during PBR design and operation (Pulz 2001). Moreover, PBR design can be also tailored in order to increase the illuminated area-to-volume ratio, reduce the light path, and increase the frequency of the light–dark cycles, with the subsequent increase in microalgae productivity and CO_2 removal rates (Pulz 2001; Richmond 2004). In this context, the shorter the light path is, the higher the frequency of the light–dark cycles and the photosynthetic rates. These frequencies also depend on the optimal cell density (OCD) in the cultivation broth due to the increased mutual shading at increasing microalgae concentrations

(Richmond 2004; Tredici 2009). Since the OCD and light path are inversely correlated, PBRs with narrow light path (i.e., 1–2 cm) and high irradiances can support high-density cultures (Zou et al. 2000). The combination of both environmental and operational parameters, together with the selection of the optimum microbial strain, determines the CO_2 capture potential, which can be estimated from microalgae productivities by applying the stoichiometric CO_2 requirement factor for microalgae growth of 1.85 g $CO_2 g^{-1}$ biomass (Table 3) (Carvalho et al. 2006; Posten 2009). The main PBR configurations will be discussed following the traditional classification into open and enclosed systems.

Open photobioreactors

Open ponds are the simplest and cheapest technology for microalgae cultivation and can be classified into natural water bodies (lakes, lagoons, or ponds) or artificial ponds (Singh and Sharma 2012). Of them, raceway ponds, also named as high rate algal ponds (HRAP), are the most applied configuration due to their higher microalgal productivities (compared to other open alternatives) at a reasonable energy cost (200 $MJ ha^{-1} day^{-1}$ or 0.03–0.2 $W m^{-3}$ for mixing) (Tredici 2009). In these HRAPs, the microalgae broth is continuously recirculated around a closed loop channel using a rotating paddlewheel (the most cost-effective mixing mode), while CO_2 (or air) can be injected at different locations of the PBR via CO_2 diffusion pumps or external CO_2 bubble columns (Fig. 5a) (Xu et al. 2009; Muñoz et al. 2012). The main advantages of HRAPs are their simplicity of construction and operation and their lower investment (in the range of 2.3–20€ m^{-2}) and operating costs compared to enclosed PBRs (Lundquist et al. 2010; Craggs et al. 2012). However, open configurations present critical disadvantages inherent to their design such as a high vulnerability to external contamination with undesired wild microalgae species or predators, a poor light utilization as a result of the low light–dark frequencies supported by the hydrodynamics of the ponds, a high water footprint by evaporation (up to 40 $L m^{-2} day^{-1}$ in desertic climates) (Massey University 2011, large land requirements, and low CO_2 transfer efficiencies as a result of the technical limitations for CO_2 supply (Xu et al. 2009). Overall, open ponds support lower biomass productivities than enclosed PBRs (Table 3) and, therefore, a lower potential for CO_2 capture (Ugwu et al. 2008). Nevertheless, despite the previously mentioned limitations, open ponds still hold a promising potential for CO_2 capture in particular applications such as biogas upgrading (the process of enriching biogas in CH_4 by removing CO_2 and H_2S). For instance, Muñoz et al. (2012) achieved removal efficiencies of 90 % for CO_2 and 100 % for H_2S in a HRAP coupled with an independent bubble absorption column (60 cm depth) where the microalgae broth was continuously recycled. Likewise, Mandeno et al. (2005) achieved reductions in the CO_2 content of biogas from 40 to 50 % by sparging the biogas into a HRAP in a countercurrent pit to improve CO_2 mass transfer (Mandeno et al. 2005). Despite presenting a lower potential for CO_2 fixation (up to 0.20 g $CO_2 L^{-1} day^{-1}$) than their enclosed counterparts, HRAPs are

Table 3 CO_2 capture potential for different PBR configurations

Reactor type	Strain	Biomass productivity ($g L^{-1} day^{-1}$)	CO_2 capture ($g L^{-1} day^{-1}$)	Reactor volume (L)	Culture conditions	Reference
Raceway open ponds	Generic	0.06–0.1	0.12–0.20	–	Outdoor sunlight	Pulz (2001)
HRAP (treating piggery wastewater)	Mixed culture	0.083	0.15	464	Outdoor sunlight	De Godos et al. (2009)
Bubble column	*Anabaena* sp.	0.86	1.45	18–90	Indoor white lamp	González López et al. (2009)
Vertical tubular (anular)	*Tetraselmis suecica*	0.42	0.78	120	Outdoor sunlight	Chini et al. (2006)
Dome reactor	*Chlorococcum litorale*	0.095	0.18	130	Outdoor sunlight	Sato et al. (2006)
Flat plate	*Chlorella* sp. HA-1	0.61	1.13	100	Indoor metal halide lamp	Morita et al. (2000)
Flat plate	Not specified	0.5	0.92	35–135	Outdoor sunlight	Posten (2009)
Horizontal tubular	*Phaeodactylum tricornutum*	1.2	2.22	200	Outdoor sunlight	Acién Fernández et al. (2001)
Horizontal tubular	*Phaeodactylum tricornutum*	2.47	4.57	50	Outdoor sunlight	Sobczuk et al. (2000)
Helical tubular	*Phaeodactylum tricornutum*	1.4	2.59	75	Outdoor sunlight	Hall et al. (2003)
Helical tubular	*Chlorella sorokiniana*	1.5	2.77	12	Outdoor sunlight	Morita et al. (2002)

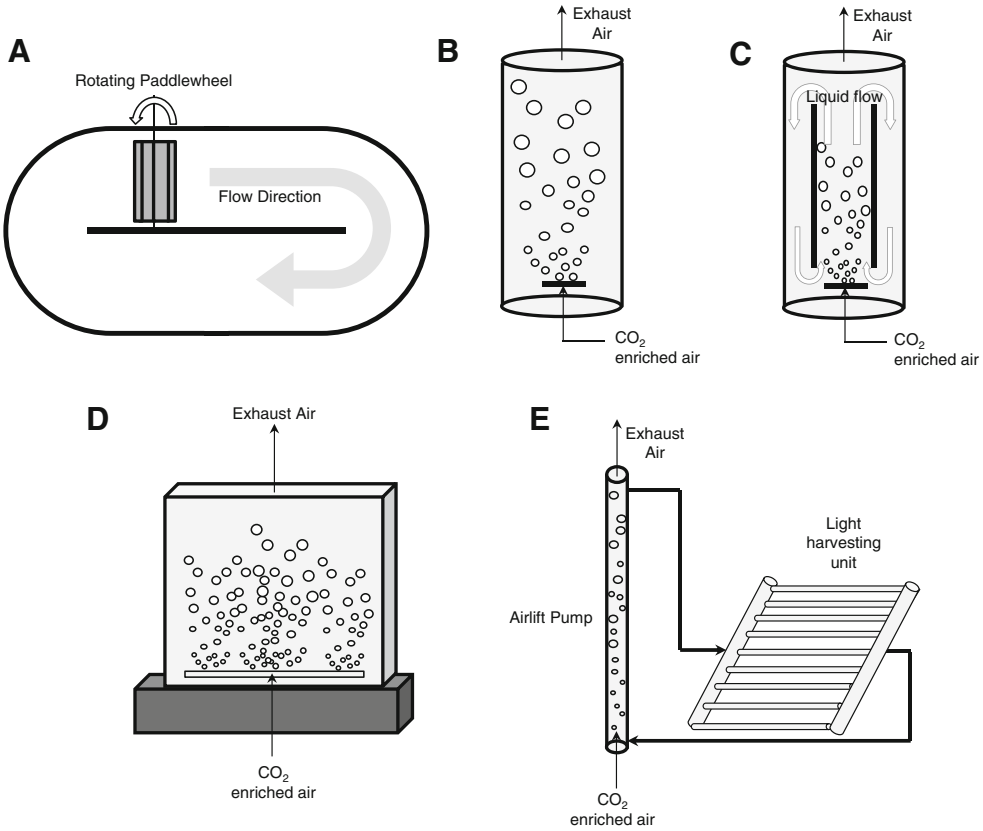

Fig. 5 Schematic configurations of PBRs for CO_2 abatement: HRAP (**a**), vertical bubble column (**b**), vertical airlift (**c**), flat-plate (**d**), and horizontal tubular (**e**) PBRs

the PBRs with the highest ratio of CO_2 fixed/CO_2 emitted (≈90.6 kg CO_2 fixed kg^{-1} CO_2 emitted, considering an energy consumption of 0.02 kWh kg^{-1} CO_2 assimilated and the average EU-27 specific CO_2 emission factor of 0.46 tonnes CO_2 emitted MWh^{-1}) (Covenant of Mayors 2012).

Enclosed bioreactors

Enclosed PBRs are more efficient at maintaining axenic microalgae cultures, allow for a better control over the process variables (temperature, pH, and CO_2 concentration), and minimize both CO_2 and water losses (Singh and Sharma 2012). In order to improve light penetration and minimize photoinhibition effect, enclosed PBRs present high illuminated area-to-volume ratios (30–70 m^{-1} in enclosed systems vs 3–10 m^{-1} in HRAPs). In enclosed PBRs, CO_2 is supplied at high concentrations (even pure CO_2 is directly supplied) by means of high-performance diffusion systems at certain locations of the PBR or directly injected in the recirculating cultivation broth to avoid inorganic carbon limitations since most PBRs are always designed considering light supply as the limiting parameter for microalgae growth (Carvalho et al. 2006). Finally, the cultivation broth must be mixed with minimum energy requirements to prevent microalgae settling and facilitate the access of microalgae cells to the photic zone of the culture, while avoiding cell damage by excessive shear stress (Carvalho et al. 2006; Posten 2009). Enclosed PBRs are classified into three major categories, depending on their configuration:

1. Vertical tubular reactors consists of a vertical pipe made of transparent materials such as polyethylene or glass and where a CO_2-enriched gas is sparged into fine bubbles at the bottom of the column for CO_2 supply and culture mixing (Kumar et al. 2011). Typical area-to-volume ratios in these systems are in the range of 10 to 30 m^{-1} (Sánchez Mirón et al. 1999). If the liquid flow is essentially random, the vertical PBR is a bubble column (Fig. 5b). On the other hand, if a concentric tube is installed inside the vertical column (namely, riser) and the CO_2-enriched gas is sparged inside the riser creating a recirculating flow pattern (upwards in the riser and downwards in the downcomer), the PBRs are named airlift PBRs (Fig. 5c).

   Vertical tubular PBRs are compact and low-cost alternatives in terms of investment cost, and some PBRs include dome or annular configurations in order to minimize the dark zones, since the low illuminated surface area is their main drawback (Morweiser et al. 2010). The energy input required ranges from 50 to 70 $W m^{-3}$ (Béchet et al. 2012). Vertical tubular PBRs provide an average potential for CO_2 capture higher than open ponds, but lower than that of their horizontal

counterparts. A recent study reported a maximum CO_2 fixation rate of 0.97 $gL^{-1}day^{-1}$ in a 3-L bubble column PBR using the microalga *Scenedesmus obtusiusculus* (Toledo-Cervantes et al. 2013), while CO_2 capture rates of up to5.4 $gL^{-1}day^{-1}$ were recorded for *Aphanothece microscopica* Nägeli in the same type of PBR (Jacob-Lopes et al. 2009). The high variability of these results confirms the high impact of the strain and the operational conditions on the PBR potential. Furthermore, estimated CO_2 capture rates of up to 1.45 g CO_2 L^{-1} day^{-1} have been achieved in column PBRs operated with the cyanobacteria *Anabaena* (González López et al. 2009) (Table 3). At these CO_2 fixation rates in vertical tubular PBRs, the ratio of kilograms of CO_2 fixed to kilograms of CO_2 emitted can be estimated to be 1.9 (Covenant of Mayors 2012).

2. Flat-plate PBRs are similar to the vertical tubular PBRs described previously but are designed to minimize the light path and to provide a homogeneous light penetration. Flat prisms between 3 and 10 cm deep with a surface area of ≈1–2 m^2 made of a transparent material are employed, which provide the high illuminated area-to-volume ratios (20–40 m^{-1}) needed to achieve high photosynthetic efficiencies and, therefore, high CO_2 removal rates (Fig. 5d) (Tredici and Zittelli 1998; Barbosa et al. 2005). Gas sparging at the bottom is employed for both pneumatic mixing and CO_2 supply, with energy consumptions similar to those of vertical tubular configurations, although alternative agitation methods consisting of panel rotation have been implemented (Kumar et al. 2011). Flat-plate PBRs are mainly illuminated on one side and can be arranged in optimal angles facing solar irradiation to maximize microalgae growth (Xu et al. 2009). Recently, new configurations such as alveolar and V-shaped panels have been implemented, resulting in increased microalgae productivities (Carvalho et al. 2006). On the other hand, flat-plate PBRs require high land areas and supporting structures when many replicate units are installed in full-scale applications (Ugwu et al. 2008). The productivities and, therefore, the CO_2 capture rates in flat-plate PBRs are similar to those recorded in vertical tubular reactors (≈1 g $CO_2L^{-1}day^{-1}$) but 10 times higher than that in HRAPs (Posten 2009; Morita et al. 2000) (Table 3). Besides, flat-plate PBRs possess ratios of 1.46 kg CO_2 $fixedkg^{-1}$ CO_2 emitted (Covenant of Mayors 2012).
3. Horizontal tubular PBRs consist of a set of horizontal transparent tubes arranged in parallel, closed loop, coiled around a hollow cylinder, or α-shape, acting as light collector (Carvalho et al. 2006; Merchuk et al. 2007; Kumar et al. 2011). They are usually equipped with a centrifugal pump or an airlift system to provide adequate flow and mixing, with the airlift systems being employed for the cultivation of shear-sensitive microalgae (Fig. 5e). Gas exchange takes place in the tubes or in especially dedicated CO_2 absorption units. The high illuminated area-to-volume ratios (45–70 m^{-1}) result in high biomass productivities (Tredici and Zittelli 1998). The large pH, CO_2, and O_2 gradients in long tubes and fouling have been pointed out as the major causes of process failures in industrial-scale facilities, while the need to maintain adequate liquid velocities in the tubes implies high energy consumption (≥100 Wm^{-3}). Strategies such as water spraying over the tubes, installation of heat exchangers, tube overlapping, and immersion of the tubes inside a pool are the most cost-effective alternatives for temperature control in outdoor facilities (Ugwu et al. 2008; Kumar et al. 2011; Singh and Sharma 2012). Horizontal tubular PBRs support the highest biomass productivities and, thus, CO_2 capture potential, with average values higher than 2 g CO_2L^{-1} day^{-1} (Acién Fernández et al. 2001; Morita et al. 2002; Hall et al. 2003), although capture values higher than 4.5 g $CO_2L^{-1}day^{-1}$ have been occasionally achieved in a tubular airlift bioreactor (Sobczuk et al. 2000). CO_2 capture rates of ≈1 g $CO_2L^{-1}day^{-1}$ have been recently recorded outdoors in a 220-L external loop airlift PBR with *Anabaena* sp. ATCC 33047 (Sánchez Fernández et al. 2012). Finally, ratios of up to 4.1 kg CO_2 $fixedkg^{-1}$ CO_2 emitted for these PBRs have been recorded, which represent the best results so far reported among enclosed PBRs (Covenant of Mayors 2012).

Despite CO_2 solubility in water being relatively high compared to that of O_2, CH_4, or N_2 (Henry's law constant of $3.4\times10^{-2}molL^{-1}atm^{-1}$), its cost-efficient supply to the microalgae broth still constitutes a large-scale technical challenge, affecting the pH and mixing in the system. Three main CO_2 supply systems have been implemented in the PBR configurations previously described: independent gas exchangers, direct gas injection to the cultivation broth, and membrane-based transfer. Among them, membrane transfer deserves special attention when CO_2 capture is the primary objective of the PBR since mass transfer in membrane units is no longer affected by the boundary layer between the gas and the aqueous phase, but a gas-permeable membrane allows CO_2 diffusion from the gas and O_2 desorption from the microalgal cultivation medium. This approach allows for reduced operating costs, since CO_2 absorption is decoupled from culture mixing, which represents a degree of freedom for process optimization (Morweiser et al. 2010). Theoretically, membrane transfer avoids CO_2 losses to the atmosphere and allows for an accurate control of the transfer rates. The use of hollow fiber membranes allows for operation at low pressure drops since no water column pressure has to be overcome by the

CO_2-laden emission. On the other hand, porous membranes provide high transfer areas but require high pressures to force the CO_2 through the membrane (especially in highly salty media), the latter implying thicker membranes and high-performance materials (Carvalho et al. 2006). A recent study reported CO_2 removal efficiencies of 85 % at a CO_2 concentration of 2 % in a hollow fiber membrane PBR (Kumar et al. 2010a). Finally, another recently proposed strategy to efficiently capture CO_2 from flue gases consists of absorbing the CO_2 in an aqueous solution, which is further purified by microalgae in a PBR. Alkaline sodium carbonate and bicarbonate solutions have been proposed as suitable solutions that can be biologically regenerated as an alternative to methyl ethyl amine, diethyl amine, or NaOH, which are used as chemical absorbents and must be regenerated by heating in highly energy-demanding processes (González López et al. 2012).

Limitations in the biological treatment of GHGs and future research needs

Despite the promising potential of biotechnologies for the abatement of CH_4, N_2O, and CO_2 emissions, their cost-efficient application is often limited by the poor mass transport of CH_4, and in a lower extent of N_2O and CO_2, from the gas to the aqueous phase due to the low aqueous solubility of these GHGs (dimensionless Henry's law constants, H, H_{CH4}=30, H_{N2O}=2, and H_{CO2}=1.2). Thus, these high H values result in low concentration gradients (low driving forces) for GHG mass transport from the gas to the aqueous phase containing or surrounding the microbial communities and, therefore, in a reduced GHG biodegradation performance (Muñoz et al. 2007). In the particular case of CH_4 and N_2O, this low mass transport entails process operation at high EBRTs, which significantly increases both the investment and operating costs of conventional biotechnologies. In PBRs, this limited mass transport restricts the implementation of a direct bubbling of the CO_2-laden streams in HRAPs and increases the volume of external CO_2 transfer units or in situ pumps. In this context, the development of innovative high-performance mass transfer approaches is mandatory. However, unlike the classical approach of improving mass transport by increasing the energy input to the bioreactor, the high-performance transport should be based on increased GHG concentration gradients (e.g., absence of aqueous phase, high cell hydrophobicity, high pH, or presence of a nonaqueous organic phase) and larger gas–cell interfacial areas.

Under mass transfer-limiting conditions, the poor knowledge of the GHG biodegradation kinetics at the trace level concentrations (almost equal to micrograms per liter) typically present in the aqueous phase when treating real emissions has also limited the correct design of bioreactors for GHG abatement (Estrada et al. 2012a). For instance, for typical emissions containing 10–200 $mg\,m^{-3}$ of CH_4 and 50–1,000 $mg\,m^{-3}$ of N_2O, microorganisms would be exposed to maximum aqueous concentrations ranging from 0.3 to 7 $\mu g\ CH_4\,L^{-1}$ and from 25 to 500 $\mu g\ N_2O\,L^{-1}$, respectively (Shimizu et al. 2000; Kampschreur et al. 2008; Girard et al. 2011; Gustavsson and la Cour Jansen 2011). In this context, it must be stressed that microbial characteristics and, in particular, microbial affinity for the target pollutant quantified as K_M and K_S play a key role on the performance of biotechnologies treating poorly soluble gaseous pollutants (Hernández et al. 2010; Rocha-Rios et al. 2011). Despite the empirical evidence for the fact that microorganisms can mineralize pollutants down to the picograms per liter level, the number of studies evaluating pollutant biodegradation at the micrograms per liter to nanograms per liter level is unfortunately scarce (Roch and Alexander 1997). Besides, the few kinetic studies reported for methanotrophs were carried out using a methodology based on the estimation of the aqueous CH_4 concentration by CH_4 headspace analyses in closed systems inoculated at high biomass concentrations and under gentle agitation, conditions which do not ensure the absence of mass transfer limitations and, therefore, the validity of the experimental data (Yoon et al. 2009). As a matter of fact, while mechanistic model predictions using the available kinetic data for methanotrophs show that CH_4 biodegradation would not be feasible at atmospheric concentrations (1.8 ppm_v), there are empirical evidence of CH_4 removal from 1.8 to 0.1 ppm_v (Whalen et al. 1990). Likewise, in the particular case of N_2O-degrading bacteria or photosynthetic microorganisms, the number of studies conducted to date is scarce. In light of the current limitations of microbiology, novel methodologies for the accurate determination of microbial GHG biodegradation kinetics at trace level concentrations must be developed. The quantification of microbial growth and the measurement of the GHG concentrations at the micrograms per liter level, in both the aqueous phase and the biofilm, constitute key analytical challenges.

The biological abatement of N_2O is also limited by the poor understanding of the microbiology governing N_2O biodegradation under aerobic conditions. The few existing studies on biological NO_x treatment (mainly NO and NO_2) were based on heterotrophic denitrification using O_2-free synthetic emissions (conditions which are far from those typically found in real N_2O-laden emissions) and autotrophic nitrification and, in most cases, were mass transfer limited (Flanagan et al. 2002). In addition, several authors have concluded that the implementation of nitrogen oxide removal based on denitrification might be limited by the need for low O_2 concentrations and the use of an exogenous

carbon source (Kalkowski and Conrad 1991; Sakurai and Sakurai 1997). In this regard, aerobic denitrification might constitute the cornerstone for the development of cost-efficient N_2O abatement processes. Thus, despite the controversy that has surrounded aerobic denitrification for years, there are nowadays consistent research findings to support the constitutive nature of some NO_3^-, NO_2^-, and N_2O reductases in bacteria such as *P. stutzeri* or *Thiosphaera pantotropha* (Robertson et al. 1995). As a matter of fact, N_2O reduction coupled to the oxidation of an electron donor (e.g., acetate) has been reported even at O_2 concentrations twice that of air saturation (Miyahara et al. 2010). However, apart from this proof of concept carried out in test tubes, aerobic denitrification has never been evaluated in a continuous bioreactor configuration, which constitutes a technological challenge in terms of electron donor supply and competition with obligate aerobic heterotrophs.

Finally, microalgae-based CO_2 capture is also limited by the low PE achieved in conventional PBRs (2–5 %) during outdoors cultivation (which significantly increases both investment and operation costs) and also by the perishable nature of microalgal biomass, which does not allow for the long-term storage of CO_2 (Acién Fernández et al. 2012b). In this context, the development of both innovative PBRs capable of minimizing the detrimental effects of photorespiration, photoinhibition, photosaturation, and temperature on PE and of low-cost microalgae harvesting technologies is crucial. Today, CO_2 capture using microalgae-based processes still exhibit high operating costs, despite being lower than those of their physical/chemical counterparts. In a recent literature review published by Acién Fernández et al. (2012b), the cost of CO_2 capture in a 100-ha facility of HRAP was estimated at $0.23 € kg^{-1} CO_2$ by using wastewater as free nutrient source and flue gases as free CO_2 source. Microalgae harvesting constitutes a significant part of the overall operating costs and is often carried out by centrifugation, filtration, coagulation–flocculation, flotation, or gravity sedimentation (Packer 2009). Full-scale algal mass production plants are often constructed with centrifugation or filtration units, despite not being recommended for small species like *Chlorella* or *Scenedesmus* (Molina Grima et al. 2003). In this context, Acién Fernández et al. (2012b) estimated the energy requirements associated to microalgae harvesting by flocculation–sedimentation followed by centrifugation in 0.1 $kWh m^{-3}$. In brief, most of the CO_2 mitigation of microalgae-based processes will actually come from the production of bioenergy from the biomass produced (with the subsequent reduction in fossil fuel consumption) and from the energy-efficient carbon and nutrients removal during wastewater treatment in PBRs (Muñoz and Guieysse 2006; Kumar et al. 2010b; Acién Fernández et al. 2012b).

Conclusions

To date, biotechnologies for GHG abatement have shown promising results in terms of elimination capacity and environmental impact. The prohibitive treatment costs and the CO_2 footprint of physical/chemical techniques, especially when dealing with large volumes of air with low GHG concentration, certainly encourage the development and application of high-performance biological methods to mitigate this global environmental problem. Despite the fact that some technical and microbiological limitations must still be overcome, the potential of biological techniques for GHG abatement has been consistently demonstrated, high removal efficiencies being so far reached mainly for CH_4 and CO_2 and in a lower extent for N_2O. In this context, the understanding of the microbiology underlying GHG biodegradation was identified as one of the most important knowledge gaps requiring further research. In addition, the development of innovative bioreactor configurations to improve both GHG mass transfer from the gas phase to the microorganisms and light supply (in the case of CO_2 abatement processes) constitutes a key research niche. Finally, the feasibility of coupling GHG biodegradation with the production of high added-value products such as PHB, single-cell protein, pharmaceuticals, or biofuels can impact positively on the overall cost-effectiveness of biological treatment processes.

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