# Chapter 9
# Remediation of Pharmaceutical and Personal Care Products (PPCPs) in Constructed Wetlands: Applicability and New Perspectives

**Ana Rita Ferreira, Alexandra Ribeiro, and Nazaré Couto**

**Abstract** Nowadays, wastewater treatment plants (WWTPs) considered not very effective in removing all types of organic compounds, including pharmaceuticals and personal care products (PPCPs). The effluent discharged containing PPCPs shows negative impact on fresh/marine waters, even at vestigial concentrations. The integration of constructed wetlands (CWs) as a biological treatment technology in WWTPs may be an option to effective removal of PPCPs, which is crucial for water bodies' protection. On the other hand, if they arrive to water bodies it is important to understand the self-restoration capacity of the system. This chapter makes an overview (based on literature and experimental data) about the effectiveness of CWs as a polishing step in WWTPs and the potential to remove contaminants if they arrive to salt marsh areas. In both cases, there is a same principle behind. CWs defined as artificially engineered ecosystems designed and constructed to control biological processes as in natural wetlands, but in a controlled natural environment.

A case study highlights the remediation potential to remove target PPCPs in both environments. Simulated CWs (spiked wastewater) planted with *Spartina maritima* and light expanded clay aggregates (LECA) as substrate. Simulated salt marsh areas (spiked elutriate soaked in sediment) were planted with the same plant but with sediment as substrate. The presence of a physical support and/or *S. maritima* decreased contaminant levels either in WWTPs or in estuarine simulated environment. Plant uptake, adsorption to plant roots/sediments and bio/rhizoremediation are strong hypothesis to explain the decrease of contaminants either in CWs or in salt marsh environment. The chapter also discusses the concept of energy production in CWs as a way to increase the competitive advantages of CWs over other treatment systems, by coupling an efficient removal together with a profitable technology, which may decrease WWTP energetic costs.

**Keywords** WWTPs • PPCPs • CWs • *Spartina maritima* • LECA

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## 9.1 Introduction

Water pollution is a relevant problem as it compromises the quality of a resource that is essential to life. In 2008, the production of hazardous chemicals (i.e., toxic chemicals defined by Eurostat) was ca.200 million tons [1]. In 2011, the European Environment Agency reported that hazardous substances, like pharmaceutical and personal care products (PPCPs), have a detrimental effect in EU fresh and marine waters [1]. PPCPs constitute a wide group of compounds largely consumed in modern societies aiming to improve the quality of daily life [2]. After utilization, e.g., pharmaceutical compounds are not completely metabolized in the body of humans and animals and as a result, metabolites, conjugates, and their native forms are excreted into the sewage system [3]. In addition, the unused and expired PPCPs are usually disposed with normal household waste or discarded into sink or toilets [4].

Wastewater treatment plants (WWTPs) receive wastewaters that contain a lot of different trace polluting compounds but are not specifically designed to eliminate all of these compounds [4–7]. Consequently, after WWTP treatment, various kinds of PPCPs and their metabolites have been detected into surface water, ground water, and even drinking water [8–12]. Upon entering the aquatic environment, and even at trace levels, PPCPs and their metabolites became a potential risk to the health of aquatic life and human beings. The available information on the ecotoxicology of these compounds is scarce, and the potential risks to the water environment are still under debate [2, 13–15]. However, it is clear that human pharmaceuticals cause e.g., antibiotic resistance in microorganisms and will negatively impact aquatic communities through feminization of male fish and affect kidneys, gills and liver in fish [13, 16].

In WWTPs, different types of treatment technologies are applied aiming to enhance organic contaminants, i.e., PPCPs removal. In fact, advanced oxidation processes, activated carbon adsorption, membrane separation, and membrane bioreactor are available to restore and maintain the chemical, physical, and biological conditions of wastewaters [17]. However, advanced treatment processes involve high capital and operational costs and selecting low-cost alternative treatments for the removal of emerging contaminants seems to be a very promising option [3, 6, 13]. Therefore, the quest for green, cost-effective, and energy sustainable technologies is a subject of debate today.

Constructed wetlands (CWs) represent an option that fits these purposes as they represent a green treatment technology, cost-effective, with low operation and maintenance requirements [18]. CWs are part of the tertiary treatment in WWTPs and may be assumed as a polishing step before the discharge for the aquatic bodies. CWs are defined as artificially engineered ecosystems designed and constructed to control biological processes as in natural wetlands, but in a controlled natural environment. CWs has been widely used to treat various kinds of wastewaters [19], such as domestic [20], agricultural [21], and industrial wastewater [22] but also storm water and acid mine drainage [23]. However, removal rate in CWs (affecting the residence time) and the effect/area of influence from the plant have been reported as limitations to this technology [6].

This chapter is an overview about the existent practices concerning PPCPs removal using CWs. The capability of a CW or a simulated salt marsh area (both planted with *Spartina maritima*) to promote the removal of two PPCPs with different physico-chemical properties, either in the presence or absence of a support matrix will also be discussed. At the end of the chapter, insights about the integration of energy production in CWs will discussed. The main aim of this concept is to increase the competitive advantages of CWs over other treatment systems, by coupling an efficient removal together with a profitable technology, which may decrease WWTP energetic costs.

## 9.2 Phytoremediation

### *9.2.1 General Aspects*

Phytoremediation is an environmentally friendly technology that uses plants for the degradation, removal, and detoxification of contaminants from soils, sediments, or waters [24]. Different mechanisms can be used to immobilize, sequester, degrade, or metabolize in place (either inside or outside the plant) depending on the type of contaminant, the site conditions, the level of cleanup required, and the type of plant [25]. The phytoremediation of organic contaminants, such as PPCPs, is complex and carried out through different approaches. The contaminant absorbed by the plant and then metabolized into nontoxic metabolites (phytodegradation). The capacity to enter into the plant depends on the lipophilicity of the pollutant. It is accepted that a Log $K_{ow}$ between 0.5 and 3 is adequate for this purpose [26]. However, contaminants can remain outside the plant. In rhizosphere, organic contaminants may be biodegraded by microorganisms that spur from root exudates (e.g., carboxylic acids, amino acids) in a synergistic action between plant and microorganisms [27]. The evolution of phytoremediation-related literature and from this, the relation with organic contaminants assessed to understand the present research tendency regarding this topic. Figure 9.1 shows the number of publications containing for the word "Phytoremediation" and then "Phytoremediation AND organic contaminants." The data was obtained from the Scopus database with the search field text = (Phytoremediation AND Organic contaminants) from 2000 to 2014. The results were refined based on: type of Literature = (Article OR Review) and subject area = (Life Sciences). The results show that the phytoremediation is intensively studied but literature regarding phytoremediation of organic contaminants represents a small percentage (between 32% in 2000 and 16% in 2014). The interest regarding phytoremediation of organic contaminants is less than the researches in phytoremediation of other organic compounds. Nevertheless, there is a growing

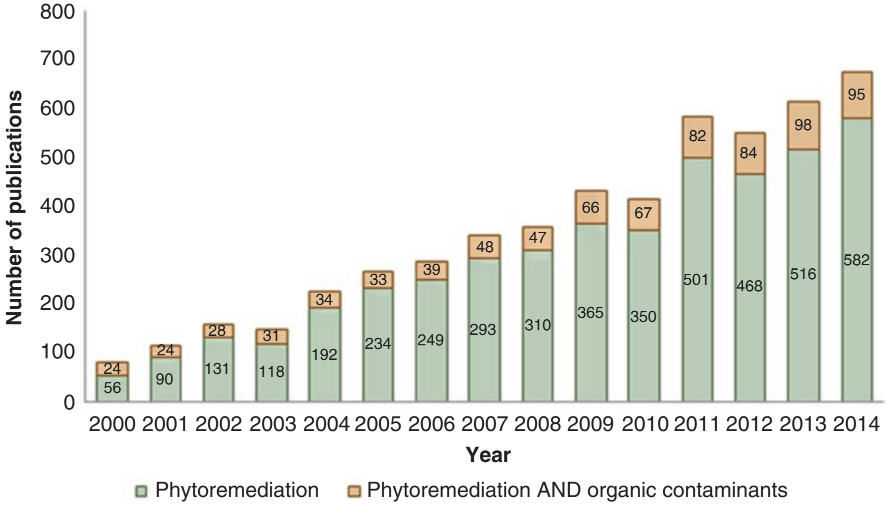

**Fig. 9.1** Number of articles or reviews published on the phytoremediation area from 2000 to 2014 (Source: online version of Scopus database accessed in 26.11.2015; search field: Phytoremediation AND Organic contaminants)

tendency regarding the studies with phytoremediation and organic contaminants (including PPCPs) (passing from 24 studies in 2000 to a maximum of 98 in 2013).

## 9.3 Constructed Wetlands

### *9.3.1 General Aspects*

CWs have been widely employed since its first full-scale application in the late 1960s. During the last five decades, CWs have evolved from empirical research into success, increasingly more popular applications, e.g., habitat restoration for native and migratory wildlife, anthropogenic discharge for wastewater, storm water runoff, sewage treatment, land reclamation following mining or refineries [28]. The CWs, also known as engineered wetlands, are designed to mimic the process involved in natural wetland systems but within a more controlled environment [18]. Physico-chemical properties of wetlands provide many positive attributes for contaminants remediation [29]. In sequence, CWs have also demonstrated to be a sustainable and operational technology to include in conventional WWTPs aiming for an efficient decrease of total suspended solids, biochemical oxygen demand (BOD), or elimination/decrease of various pollutants including nitrogen, phosphorus and heavy metals [30]. In recent years, the applicability of CWs for the remediation of PPCPs has been increasingly explored and proved to be successful for a variety of compounds with a simultaneous improvement of water quality [31–36].

CWs can be classified according to their hydrology (free water surface, subsurface flow, and hybrid), flow path (horizontal or vertical), and types of macrophyte (free-floating, emergent, and submerged) [6, 37]. According to the review of application of CWs for wastewater treatment in developing countries performed by Zhang et al. (2014) [38] horizontal subsurface flow (HSSF) CWs have been the most frequently employed aquatic plant-based systems to remove pharmaceutical compounds although vertical subsurface flow (VSSF) CWs and hybrid CWs have also shown good removal efficiencies for pharmaceuticals. The treatment performance in CWs is critically dependent on the optimal operating parameters and includes water depth, hydraulic load, hydraulic retention time, and feeding mode related to the sustainable operation for wastewater treatments [18]. The contaminants removal in wastewater involves a set of abiotic and biotic processes influenced by plants, substrate, and associated microbial assemblages, which assist in integral contaminant removal, while the more homogeneous conditions in WWTPs (without these dynamic interactions) induce fewer degradation pathways [30]. The physico-chemical processes contributing to contaminants degradation in CWs have not been thoroughly described [39] and it is imperative to understand the transformation processes that driven PPCPs removal, aiming to optimize CWs design for an effective contaminants removal.

CWs have advantages over the natural wetlands but also have some limiting factors. Land requirement is a limiting factor for their broader application, especially in regions where land resources are scarce and population density is high. In addition, the biological components can be sensitive to toxic chemicals (e.g., ammonia and pesticides) and peaks of contaminants in water flow may temporarily reduce treatment effectiveness. Another point is the possible re-entry of contaminants after the death of plants, which may result in a poor removal performance of CWs. To prevent this, it is necessary to develop an appropriate plant harvest strategy, with a focus on the reclamation and recycling of plant resources in CWs.

### *9.3.2 Salt Marsh Plants*

The role of plants in CWs has been frequently discussed and several studies state their crucial role, being considered the essential component of the design of CW treatments [38]. The roots maintain the hydraulic properties of the substrate, and the shoots protect the surface from erosion while shading prevents algae growth. Besides, plants play another important role in stimulating the development and activities of microbial populations, which are supported by the rhizodeposition products (i.e., exudates) promoting the occurrence of various biological processes in the rhizosphere (e.g., transformation and mineralization of nutrients and organic pollutants) [40]. Not all plants are suitable for waste treatment since plants must be able to tolerate the combination of continuous flooding and exposure to waste streams containing relatively high and often variable concentrations of

**Table 9.1** Salt marsh species reported for PPCPs removal from aquatic medium

| Plants | PPCPs | References |
|---|---|---|
| *Typha spp.* | Carbamazepine, clofibric acid, and ibuprofen | [36] |
| *Typha angustifolia* | Triclosan | [44] |
| | Ibuprofen, diclofenac, caffeine, and methyl dihydrojasmonate | [39] |
| *Scirpus spp.* | Carbamazepine, ibuprofen, naproxen, tramadol | [8] |
| *Scirpus validus* | Caffeine | [45] |
| | Carbamazepine | [46] |
| *Phragmites australis* | Enrofloxacin, ceftiofur, and tetracycline | [47] |
| | Ibuprofen, naproxen, diclofenac, tonalide, and bisphenol A | [48] |
| | Ibuprofen, diclofenac, caffeine, and methyl dihydrojasmonate | [39] |
| *Typha* and *Phragmites* | Clofibric acid, carbamazepine, caffeine, methyl dihydrojasmonate, galaxolide, tonalide, ibuprofen, naproxen, ketoprofen, and diclofenac | [33] |

contaminants [41]. Therefore, the study of plant species is crucial to obtain better treatment efficiency in CWs.

Salt marsh plant species are morphologically adapted to cope with environmental stress, such as, high concentrations of salt and/or insufficient water conditions. In wetlands, these types of plants have been reported to be one of the main factors influencing water quality by their capability of utilizing nitrogen, phosphorous, and other nutrients [18]. Salt marsh plants also have shown potential to remediate inorganic [42] and organic [43] contaminants. Table 9.1 summarizes studies using salt marsh plants for PPCPs removal in aquatic media simulation. The most popular salt marsh plants are *Phragmites australis*, *Typha* spp., including *Typha angustifolia*.

### *9.3.3 Substrates*

Substrate or support matrix is considered as an important component of CWs that provides a suitable growth medium for plant and microorganisms together with a successful movement of wastewater [49]. The frequently used substrates include natural (sand, gravel, clay), artificial (light weight aggregates, activated carbon), and industrial (slag) materials [18]. Substrates can remove contaminants from wastewater by exchange, adsorption, precipitation, and complexation [36]. For this reason, the chosen materials are extremely important when designing CWs as, e.g., a material with high sorption capacity will improve contaminants removal [50]. Calheiros et al. [49] studied the treatment of tannery wastewater by *Typha latifolia* in CWs established with three different substrates. The tested substrates proved to be adequate for *T. latifolia* development with higher organic removal for the two expanded clay aggregates when compared to the fine gravel. Dordio et al. [51] showed in laboratorial batch experiments that light expanded clay aggregate (LECA) is considered a good sorbent for acidic (e.g., clofibric acid and ibuprofen) and neutral pharmaceutical compounds (carbamazepine) with removal efficiencies between 75% and 97%. Recently, biosorbents such as rice husk, pine bark, and granulated cork have also been considered as interesting alternatives to the common substrate materials in CWs due to their low cost, economical value of reuse, and easy disposal by incineration certain [6].

## 9.4 Case Study

The aiming of this study was to understand, in the tested conditions, the remediation potential of the different components of the system (plant, substrate) after a (simulated) PPCPs contamination before (CWs) and after effluent discharge (salt marsh area). In addition, the capacity of planted CWs and LECA as a support medium to remove contaminants were also evaluated. The first study tested the potential of CWs for PPCPs removal and the second simulates the self-restoration capacity of the salt marsh area affected by PPCPs load. In both cases, *S. maritima* was the chosen plant species. This plant species is frequently found in Portuguese estuaries and may potentially be used in CWs. Two PPCPs with different physico-chemical properties were chosen: caffeine (CAF) and oxybenzone (HMB). CAF has a Log $K_{ow}$ of −0.77, pKa of 10.4, and solubility of $2.16*10^4$ mg $L^{-1}$ at 25 °C. CAF is one of the most consumed stimulant of central nervous system worldwide [45]. HMB is a UV filter increasingly used in personal care products, in particular as light-filters to protect the human skin from harmful exposure to UV irradiation [52]. HMB has a Log $K_{ow}$ of 3.8, pKa of 7.6, and solubility of 69 mg $L^{-1}$.

### *9.4.1 Methodology*

The work was divided into two different parts: [53, 54]. For sake of clarity, a comparative assessment between both is carried out. Experimental design of the work is shown in Fig. 9.2.

CWs were prepared with LECA as substrate and with continuous entry of contaminants, simulating real operating parameters (residence time; Assay 1). Simulation of the salt marsh environment was carried out with sediment soaked in the respective elutriate, allowing simulation of nutrients and contaminants exchange among plants, solution, and sediment, as occurs in the natural environment (Assay 2). The effluent was collected after a secondary treatment stage in a WWTP from *Águas de Lisboa e Vale do Tejo* located in Quinta do Conde, Sesimbra, Portugal

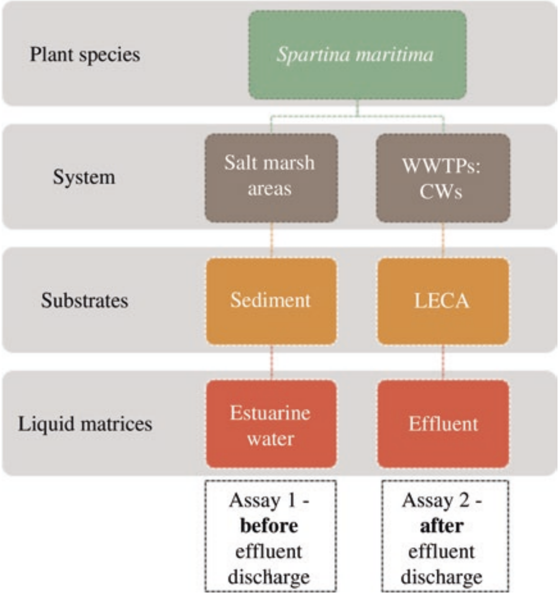

**Fig. 9.2** Experimental design of the work

(38°34’13”N, 9°2’7” W). The plants, water, and colonized sediment were collected at low tide from a salt marsh, located in the Tagus River Estuary, Portugal (38º36’59.39”N; 9º02’33.41”W).

All the microcosms where wrapped in aluminum foil to protect of the sunlight and simulate real light penetration conditions. Groups of *S. maritima* were homogeneously distributed (9.0 ± 1.0 g) by different treatments and exposed to the medium (wastewater and elutriate). Plant roots were disinfected before the experiments to stop bacterial activity. The experiments to simulate CWs were carried out for 7 days, but there was three spiking periods (at days 0, 3, and 6) making the concentrations range from 0.5 mg $L^{-1}$ to 1.5 mg $L^{-1}$. The experiments to simulate the salt marsh area were carried out for 10 days, and the system was spiked with 1 mg $L^{-1}$ of each contaminant. The purpose of different spiking periods is to simulate a successive load of contaminants in CWs and a lower contaminant load in estuarine systems. Three types of controls carried out in parallel (spiked matrix with isolated presence of substrate or plant and non-spiked matrix with the presence of plant to evaluate plant vitality). Photosynthetic pigments used to evaluate plant vitality when exposed to contamination. High performance liquid chromatography (HPLC) used to quantify the levels of different contaminants in the studied matrices.

**Table 9.2** Potential of remediation of plant and substrate

| | CW | | | Salt marsh area | | |
|---|---|---|---|---|---|---|
| | Plant | | Substrate | Plant | | Substrate |
| Contaminant | *S. maritima* vs. control[a] | Planted vs. unplanted | Unplanted LECA bed vs. control[a] | *S. maritima* vs. control[b] | Planted vs. unplanted | Unplanted vs. control[b] |
| CAF | (=) 0% | (+) 20% | (−) 40% | (=) 0% | (+) 19% | (+) 17% |
| HMB | (+) 10% | (=) 0% | (+) 10% | (+) 60% | (+) 38% | (+) 60% |

Note: (+), (−) or (=) means the potential of the plant or substrate comparing (vs.) with controls

[a] Control only with wastewater

[b] Control only with elutriate

### 9.4.2 Results and Discussion

The presence of contaminants may influence the functions of plants and associated efficiency for contaminants removal. The evaluation of chlorophylls (*a* and *b*) and carotenoids ($\mu g\ g^{-1}$) of *S. maritima* exposed to PPCPs showed that this plant tolerates up to 1.5 mg $L^{-1}$ of CAF and HMB. Table 9.2 shows the remediation potential of the system components (plant and substrates: LECA and sediment) in each simulation environment (CWs and salt marsh areas) compared with respective controls. In the CW, the presence of *S. maritima* only increased HMB remediation by 10% but did not have any effect on CAF. Also, in the simulated salt marsh area *S. maritima* had no effect on CAF remediation but promoted a decrease of 60% in HMB. *S. maritima* promoted CAF remediation in about 20% with the presence of LECA (CWs) or sediment (salt marsh area). HMB presented a different remediation behavior. The remediation was neglectable in CWs (plant, wastewater, and LECA) and was almost 40% in simulated salt marsh area (plant, elutriate and sediment). Regarding the susbtrates, the presence of sediment enhanced the remediation of HMB by 60% and of CAF by 17% in salt marsh simulation. In wastewater, LECA presented 10% of HMB remediation, but negatively affected CAF remediation.

The uptake by plants is more probable for compounds with Log $K_{ow}$ values of 0.5–3 [26]. Recent studies show that compounds with other Log $K_{ow}$ values may also enter the plant. Wu et al. (2013) [55] detected PPCPs with a detection frequency of 64%, and concentrations range of 0.01–3.87 ng $g^{-1}$ (dry weight) in vegetables. Triclocarban, triclosan, and fluoxetine (Log $K_{ow} > 3$) accumulated in roots at levels higher than the other PPCPs, while translocation to leaves/stems was for compounds with Log $K_{ow} < 3$, e.g., carbamazepine. Also, (ab)/adsorption to plant roots and (bio)/rhizoremediation in liquid phase or substrate may be strong hypothesis to the enhanced remediation in the tested conditions. The higher removal of HMB, compared to CAF, explained by their octanol water partition coefficient (Log $K_{ow} > 3$) and solubility, which promotes their retention by adsorption of the solid matrices (bioconcentration in the roots or in the sediment through adsorption processes, which is higher for hydrophobic contaminants). CAF has a very high solubility and tends to remain in the liquid phase. Therefore, the presence of microorganisms (either in simulated salt marsh area or CW/liquid or solid phase) appears to favor biodegradation. The studied compounds are reported as biodegradable, being indicated as readily biodegradable, mainly HMB [56, 57].

## 9.5 CWs Coupling Plant Microbial Fuel Cells

The combined/integrated treatment systems present a novel pathway to improving CWs functions. The improvement of wastewater quality with simultaneous energy recovery has garnered much attention in recent years [58]. Plant microbial fuel cell (Plant-MFC) is an emerging technology, which consists in the conversion of solar energy to bioelectricity. It was patented in 2007, and the proof-of-principle was published in 2008 (e.g., [59]) and developed in an EU project 2009–2012 resulting from a spin-off company Plant-e. Plant-MFC may represent an add-in value to CWs. 50% of photosynthetic organic matter goes to soil where naturally occurring bacteria oxidize it and transfer energy rich electrons to the anode of the fuel cell. The energy can be used as electrical energy [60]. In addition, plants transfer oxygen to the rhizosphere through the root system and enhance the aerobic degradation of unutilized organic matter, nitrification and mineralization of aromatic amines [61]. Figure 9.3a presents a model of the plant-MFC. The maximum and long-term (2 weeks) power output of best performing Plant-MFC reached 0.44 and 0.222 W $m^{-2}$ [60], a value comparable with conventional biomass–electricity chains, with potential to cover energy consumption. The technology has been scaled up to 25 $m^2$ in a “green electricity roof” and has a potential to be applied in wetlands [62]. In the case of CWs the “traditional” approaches, the anodic chamber is in the bottom region of the system (Fig. 9.3b).

In this region, microbes oxidize the organic matter and promote denitrification thus generating electrons ($e^-$), protons ($H^+$), and carbon dioxide. Electrical current is generated when the electrons migrate to the cathode. The voltage difference between the anode and cathode, together with the electron flow in the outer circuit, generate electrical power [63]. The electrons from the anode also react with oxygen (or other electron acceptors) at the cathode to produce water and other reduced compound. Different electrode materials can be used for the process (e.g., stainless steel mess, platinum, carbon paper, and granular active carbon). Carbon and graphite are commonly used as anode and cathode electrode materials because they offer high electrical conductivity and non-oxidative nature thus offering a good medium for the attachment and growth of microbial communities [64]. It is important to note that various operation parameters and designs have been developed lately by coupling MFC into other wastewater treatment process in an attempt to maximize the aerobic and anaerobic conditions. Different configurations can be found in the following references: [58, 65–67]. The study of the Plant-MFC concept extensively explored while the integration of CW and MFC is still in the beginning. Combining CW and MFC seems a promising green technology to be incorporated in WWTPs

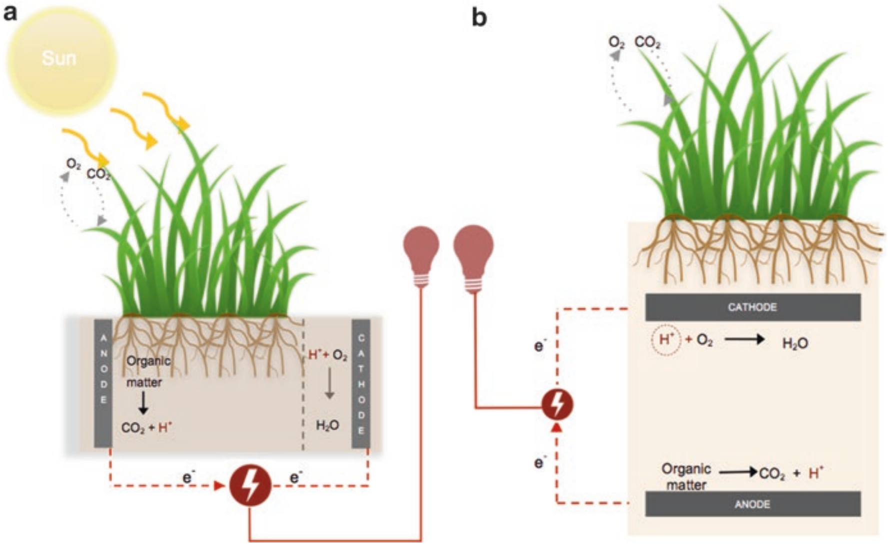

**Fig. 9.3** Schematic diagram of (**a**) model of a plant microbial fuel cell producing electricity and driving a light source (adapted from [59]); (**b**) model of constructed wetland including the concept of microbial fuel cell (adapted from [67])

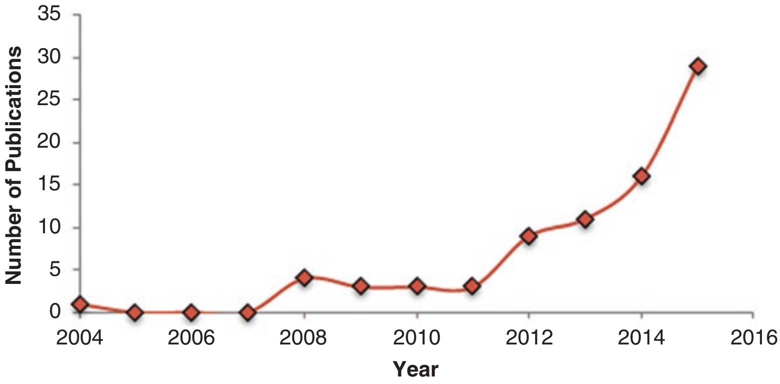

**Fig. 9.4** Publications from 2004 to 2015 (Source: online version of Scopus database accessed in 26.11.2015; Search terms: Constructed wetlands AND Microbial fuel cells; Search field: Article Title, Abstract, Keywords; Document type: Article or Review)

allowing a cost-effective process to produce electricity. Several works using this technology to remove organic contaminants from wastewater with simultaneous energy production have been reported. Some examples are given below.

Figure 9.4 shows the increased number of publications with the integration of CWs and MFC, retrieved from Scopus (26 November 2015). In the online version of Scopus database, the search terms text = (Constructed wetlands AND Microbial fuel cells) with a search field: Article Title, Abstract, Keywords in a period between 2004 and 2015, were used. The results were further refined based on: type of Literature = (Article OR Review) and subject area = (Life Sciences). The study carried out by Villasenor et al. [68] operated into a HFCW-MFC using a bentonite layer to separate the lower anaerobic anode compartment and the upper aerobic cathode compartment. It was reported 95% of COD removal (mean influent concentration of 560 mg $L^{-1}$) and a power density of 20.76 mW $m^{-2}$in the CW. These authors reported that several factors influenced the electricity generation, such as the aerobic environment in the upper wetland zone, which in part, depends on the aeration potential of the plants. In general, the aeration potential of macrophytes is rather low compared with the conventional aeration systems in wastewater treatment plants.

The authors Zhao et al. [58] studied CW-MFC to treat swine wastewater operated in batch mode, in continuous, without and with air diffusion heads to aerate the cathode region. 71.5% of COD was removed (with initial concentration of 3190–7080 mg $L^{-1}$) and a peak power density of 12.83 mW $m^{-2}$was produced. The aeration in the cathode region significantly enhanced the performance of the CW-MFC, with the continuous mode demonstrating an average of 76.5% COD removal (average influent COD concentration of 1058.45 ± 420.89 mg $L^{-1}$) and a peak power density of 9.4 mW $m^{-2}$. Doherty et al. [66] studied the ability of the alum-sludge-based CW-MFC to remove organics from wastewater while producing electricity with different flow directions on the CW-MFC performance. They concluded that the flow direction influenced the efficiency of the system. The authors say that the simultaneous upflow–downflow CW-MFC combats the two major bottlenecks of CW-MFC power output: reducing the separation between the electrodes and maintaining anoxic conditions at the anode and aerobic conditions at the cathode.

Fang et al. [69] applied a vertical CW-MFC system to treat azo dye wastewater (aromatic compounds) and simultaneously produced electricity. The system achieved 91% of decolorization rate and a voltage output of about 610 mV. The results obtained by these authors showed that plants grown in cathode region had potential to enhance the voltage output and slightly promoted dye decolorization efficiency. Villaseñor et al. [68] reported the influence of plants in voltage, stated that photosynthetic activity affected the redox conditions in the cathode compartment, as the deposition of organic matter and $O_2$ in the rhizosphere increased. During the night, the voltage dropped to approximately 200 mV in the horizontal flow CW-MFC, planted with *Phragmites australis*, and gradually increased to maximum values during daylight. Liu et al. [61] have also shown the importance of plants in power density and nutrient removal of CW-MFC. The authors incorporated the root exudates of *Ipomoea aquatica* as part of fuel into the anode section of the CW-MFC and produced a power density 142% higher than that of 5.13 mW obtained from the unplanted systems. They also promoted the reduction of internal resistance. The planted CW-MFC removed 95% of COD whereas 92% of removal achieved in the unplanted CW-MFC. The average nitrogen removal efficiencies were 54% and 91% in the unplanted and planted systems, respectively. The concept of CWs coupled to MFC systems was tested with *Typha latifolia* [67]. Electricity was generated with maximum power density of 6.12 mW $m^{-2}$ and contaminant removal was enhanced during wastewater treatment. The removal efficiencies of COD, $NO^{-}_{3}$, $NH^{+}_{4}$ were of 100%, 40%, and 91%, respectively. Despite the several studies, the combination of CW-PMFC is an emerging technology and more research is required to increase the power output (as nowadays it is too low to be directly utilized) [70].

## 9.6 Conclusions

Population growth implies higher and faster generation of WWTP waste streams as well as higher consumption of PPCPs. These compounds are not efficiently removed in WWTP treatment methodologies and the effluent discharge into water bodies may lead to environmental and human risks. There is a need to find sustainable solutions to prevent this situation in future (by acting in WWTPs) or to remediation areas that have been contaminated throughout the times (salt marsh areas). In both environments, it is important to study the importance of "key-components" in the system, i.e., matrix, plant species and substrates. The remediation capacity of the system results from a dynamic interaction between matrix-plant-substrate components and physico-chemical properties of the PPCPs, which will promote their dispersion/dilution in liquid fraction, adsorption to solid fraction, or bio−/ rhizoremediation. The concept of CWs as a green technology to remediate organic contaminants matches the purpose of Plant-MFC with the associated benefit of electricity.

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