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# 1 Biodegradation of polycyclic aromatic hydrocarbons: using microbial 2 bioelectrochemical systems to overcome an impasse

3 **Maria Kronenberg<sup>a</sup>, Eric Trably<sup>a</sup>, Nicolas Bernet<sup>a</sup>, Dominique Patureau<sup>a</sup>**

4 <sup>a</sup> LBE, INRA, 102 avenue des Etangs, 11100 Narbonne, France, izabel.kronenberg@supagro.inra.fr

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21

## 22 Abstract

23 Polycyclic aromatic hydrocarbons (PAHs) are hardly biodegradable carcinogenic organic compounds.  
24 Bioremediation is a commonly used method for treating PAH contaminated environments such as soils,  
25 sediment, water bodies and wastewater. However, bioremediation has various drawbacks including the  
26 low abundance, diversity and activity of indigenous hydrocarbon degrading bacteria, their slow growth  
27 rates and especially a limited bioavailability of PAHs in the aqueous phase. Addition of nutrients,  
28 electron acceptors or co-substrates to enhance indigenous microbial activity is costly and added  
29 chemicals often diffuse away from the target compound, thus pointing out an impasse for the  
30 bioremediation of PAHs. A promising solution is the adoption of bioelectrochemical systems. They  
31 guarantee a permanent electron supply and withdrawal for microorganisms, thereby circumventing the  
32 traditional shortcomings of bioremediation. These systems combine biological treatment with  
33 electrochemical oxidation/reduction by supplying an anode and a cathode that serve as an electron  
34 exchange facility for the biocatalyst. Here, recent achievements in polycyclic aromatic hydrocarbon

35 removal using bioelectrochemical systems have been reviewed. This also concerns PAH precursors: total  
36 petroleum hydrocarbons and diesel. Removal performances of PAH biodegradation in  
37 bioelectrochemical systems are discussed, focussing on configurational parameters such as anode and  
38 cathode designs as well as environmental parameters like porosity, salinity, adsorption and conductivity  
39 of soil and sediment that affect PAH biodegradation in BESs. The still scarcely available information on  
40 microbiological aspects of bioelectrochemical PAH removal is summarised here. This comprehensive  
41 review offers a better understanding of the parameters that affect the removal of PAHs within  
42 bioelectrochemical systems. In addition, future experimental setups are proposed in order to study  
43 syntrophic relationships between PAH degraders and exoelectrogens. This synopsis can help as guide for  
44 researchers in their choices for future experimental designs aiming at increasing the power densities and  
45 PAH biodegradation rates using microbial bioelectrochemistry.

#### 46 **Capsule:**

47 This review can help as guide for researchers in their choices for future experimental designs aiming at  
48 increasing the power densities and polycyclic aromatic hydrocarbon biodegradation rates using microbial  
49 bioelectrochemistry.

#### 50 **Keywords:**

51 Polycyclic aromatic hydrocarbons; microbial fuel cell; microbial electrolysis cell; exoelectrogen;  
52 bioremediation

#### 53 **Abbreviations:**

54 BES: Bioelectrochemical system

55 MFC: Microbial fuel cell

56 MEC: Microbial electrolysis cell

57 PAH: Polycyclic aromatic hydrocarbon

58 HDB: Hydrocarbon degrading bacteria

## 59 **1. Introduction**

60 Polycyclic aromatic hydrocarbons (PAHs) are part of a large group of compounds characterized by a  
61 structure composed of carbon and hydrogen atoms. PAHs derive from the incomplete combustion of  
62 organic matter, i.e. from transportation fuel (Lan et al., 2016), coal mining (Yakovleva et al., 2016),  
63 emissions from power plants and petroleum spills (Lübeck et al., 2016) as well as other anthropogenic  
64 sources. All PAHs are typically “water-hating” and “fat-loving” chemicals (Jones and de Voogt, 1999) and  
65 are very difficult to biodegrade (Barrie et al., 1992). The fate of PAHs in the environment is associated  
66 with multiple abiotic and biotic processes including volatilisation, microbial and chemical transformation  
67 and sorption (Reid et al., 2000). Once these water-hating molecules are released into water bodies or  
68 soils, they have a tendency to preferentially adsorb to organic particles, thus becoming less available for

69 biological degradation in aqueous phases (Palm et al., 2004). In consequence, they are inclined to  
70 accumulate in soils (Yang et al., 2014) and sediments (Feng et al., 2012). Inside organisms they  
71 accumulate in the fatty tissues of the cell rather than the aqueous compartments where most substrate  
72 bio-transformation takes place. Hence, apart from their thermodynamic stability, the degradation of  
73 PAHs by microorganisms is an issue since their likeliness to adsorb on non-polar molecules makes them  
74 less bio-available (Huang et al., 2013; She et al., 2013) while the metabolic pathways involved in their  
75 degradation are slow (Katsoyiannis, 2016). Exposure of humans to polycyclic hydrocarbons in the  
76 environment involves inhalation of vapours or air-suspended particles, dermal contact as well as dietary  
77 ingestion (Domingo, 2004). A massive environmental and societal challenge is at stake to limit PAH  
78 bioaccumulation in the food chain since they have been widely recognized as carcinogenic, teratogenic  
79 and mutagenic contaminants (Kim et al., 2013).

## 80 **2. Limits of bioremediation of polycyclic aromatic hydrocarbons**

81 Bacteria are known to play a fundamental role in the removal of contaminants from the environment  
82 (Hatamian-Zarmi et al., 2009; Pieper and Seeger, 2008). However, considering that most contaminated  
83 sediments and soils are oxygen depleted, *in situ* bioremediation of PAHs is often associated with anoxic  
84 or anaerobic conditions. Bioventing is a technique that supplies oxygen so as to create aerobic  
85 conditions. Numerous aerobic bacteria that utilise PAHs as a carbon and energy source have been  
86 isolated (Venkata Mohan et al., 2006), thus revealing that PAHs containing 2 to 4 rings can be easily  
87 biodegraded under oxic conditions (Cerniglia, 1993). However, the delivery of oxygen to sediments has  
88 been criticized as ineffective (Cruz Viggi et al., 2015) since oxygen rapidly diffuses away from where it  
89 was applied (Zhang et al., 2010). Previous studies mainly focused on anaerobic PAH degradation by  
90 mixed cultures under nitrate, sulfate or iron reducing conditions (C.-H. Li et al., 2010a; Winderl et al.,  
91 2010; M. Xu et al., 2015). Even though certain strains for PAH removal under anaerobic conditions have  
92 been identified, the microbial degradation of PAH is still limited by five factors: (i) low abundance,  
93 diversity and activity of indigenous PAH degrading bacteria (Fagervold et al., 2005), (ii) slow growth rates  
94 of the organisms with doubling times ranging from several weeks to months (Kazumi et al., 1997;  
95 Meckenstock et al., 2004), (iii) high partial pressure of hydrogen (Christensen et al., 2004), (iv) undershot  
96 threshold concentrations of pollutants and/or pollutant specific microorganisms (Rhee et al., 2001;  
97 Young-Cheol Cho et al., 2003) and (v) rare bioavailability of PAHs in the aqueous phase (Barret et al.,  
98 2010; Venkata Mohan et al., 2006).

### 99 *How limitations of PAH bioremediation are addressed at present*

100 Research efforts consist in accelerating the indigenous microbial turnover of PAHs (Chang et al., 2003;  
101 Coates et al., 1996). On the one hand, bio-stimulated growth of naturally occurring pollutant-degrading  
102 microorganisms can be achieved by the addition of electron acceptors, co-substrates and nutrients.  
103 Electron acceptors such as nitrate, ferric ion and sulfate are used by anaerobic microbes for the  
104 discharge of electrons that they obtain from organic matter utilisation. It has been observed that nitrate  
105 amendment enriches microbial functional genes allowing for *in situ* PAH bioremediation (Xu et al., 2014).  
106 Nutrients and co-substrates, additionally, promote microorganism cell growth and enhance their  
107 bioremediation capacity. Examples include methanol and acetate that have been employed as additional

108 carbon sources for microorganisms in order to increase the natural attenuation of PAHs in a marine  
109 sediment (Zhang and Lo, 2015). Biostimulation, on the other hand, is another common approach for  
110 removing organic pollutants. However, in the case of nitrates, biostimulation leads to secondary  
111 pollution issues (Pandey and Fulekar, 2012). A limited dispersion of chemicals through the soil matrix  
112 (Anneser et al., 2010), their consumption via abiotic reactions or their diffusion away from PAHs (Chun et  
113 al., 2013; Yu et al., 2016) can decrease the efficiency of biostimulation (Jobelius et al., 2011). This implies  
114 that a periodic replenishment of chemicals renders biostimulation economically unfavourable (Mittal  
115 and Rockne, 2010). Bioaugmentation represents a third option for PAH bioremediation. This technique is  
116 based on the application of indigenous or exogenous microorganisms such as fungi (Yanto et al.,  
117 2017) or bacteria (Song et al., 2017; Trably et al., 2003) to polluted and hazardous wastes in order to  
118 accelerate the removal of PAHs (Liu et al., 2014; Payne et al., 2011). Nevertheless, as the preparation of  
119 the inoculum and the loss in microbial activity during inoculation are energy and time consuming,  
120 bioaugmentation appears to be an even less economical solution (Laszlova et al., 2016).

### 121 **3. Bioremediation of polycyclic aromatic hydrocarbons assisted by microbial** 122 **bioelectrochemical systems**

#### 123 *Basics of microbial bioelectrochemistry*

124 Microbial bioelectrochemical systems (BESs) are one or two compartment electrochemical devices in  
125 which an anode and a cathode favour redox-reactions that are catalysed by microorganisms (Allen and  
126 Bennetto, 1993): this is the electroactive biocatalyst. Electrons produced by microorganisms from  
127 organic matter oxidation are transferred to the anode and flow via a conductive material to the cathode  
128 where they are consumed by biotic or abiotic reduction reactions (Logan et al., 2006). In this way,  
129 microbes convert organic matter into electric current (Kiely et al., 2011) which can be used to drive an  
130 electrical load. The principle of bioelectrochemistry is the ability of certain microorganisms to  
131 interchange electrons with insoluble conductive materials via extracellular electron transfer (Reimers et  
132 al., 2001; Tender et al., 2008). On the anode side, these are called anode-respiring bacteria or  
133 exoelectrogens.

#### 134 *MFC and MEC*

135 The prototype of a BES is the microbial fuel cell (MFC) that generates electricity based on organic matter  
136 oxidation in the anode chamber (Venkata Mohan et al., 2014). Oxygen is traditionally used as electron-  
137 acceptor in the cathode compartment or at the air-cathode due to its unlimited availability and high  
138 standard redox potential (Bond and Lovley, 2003; Hou et al., 2012). Depending on the complexity of the  
139 substrate, typical maximum power densities of MFCs lie between 2 and 3 W/m<sup>2</sup> of projected electrode  
140 surface (mostly cathode) at optimum conditions (30°C, neutral pH, 20 mS/cm conductivity, buffered  
141 solution) (Logan and Rabaey, 2012). A rise in electrode area per volume of reactor running on  
142 wastewater achieved power densities up to 1.55 kW/m<sup>3</sup> (2.77 W/m<sup>2</sup>) (Reimers et al., 2001). MFCs can be  
143 run on inexpensive organic wastes such as wastewater, sludge and biowastes (Venkata Mohan et al.,  
144 2014), in which PAHs can be found at low concentrations. The second type of BES is the microbial  
145 electrolysis cell (MEC) that uses a small amount of energy to fuel chosen reactions in the cathode

146 chamber. In a MEC, oxygen is eliminated from the cathode chamber so that electrons released from the  
147 cathode can be exploited for other uses than oxygen reduction. Mostly, protons from aqueous solutions  
148 are reduced to hydrogen gas (Villano et al., 2010) although other terminal electron acceptors have also  
149 been suggested. These comprise chlorophenols (Kong et al., 2014), nitrobenzene (Mu et al., 2009; Wang  
150 et al., 2011), polychlorinated ethenes (Aulenta et al., 2008; Strycharz et al., 2008) and cobalt(II) (Huang  
151 et al., 2014). In most studies, it is assumed that electroactive microorganisms catalyse the oxidation and  
152 reduction reactions in the anode and cathode chambers (Jafary et al., 2015; Rozendal et al., 2008).  
153 Nevertheless, the thermodynamic reaction barrier of these reactions still needs to be circumvented with  
154 a small external voltage delivered by a power source (Sun et al., 2008) or by setting an electrode  
155 potential using a potentiostat (Logan and Rabaey, 2012).

### 156 *The application of microbial bioelectrochemistry to polycyclic aromatic hydrocarbon removal*

157 The biocatalytic principle of a BES contributes to drive thermodynamically unfavourable reactions and  
158 can thus be an alternative electron source for improving PAH removal. Recalcitrant PAHs may be more  
159 easily transformed to less complex compounds if the metabolism of PAH degraders is directly or  
160 indirectly boosted by a bioelectrochemical activity in the vicinity of the electrodes (Chandrasekhar and  
161 Venkata Mohan, 2012). As an example, in an experiment, the number of hydrocarbon-degrading bacteria  
162 (HDB) close to the anode of a MFC increased in comparison to an open circuit control when an electric  
163 current was applied (Wang et al., 2012). When research on BES began 15 years ago, scientists focused on  
164 the production of energy vectors (hydrogen or electricity) while evidence of aromatic hydrocarbon  
165 removal by BESs only appeared in 2010 (Zhang et al., 2010). Using <sup>14</sup>C-labeling, Zhang et al.  
166 demonstrated that toluene could be quantitatively oxidized to carbon dioxide in a MFC in the presence  
167 of *Geobacter metallireducens*, a popular exoelectrogenic bacteria found in numerous MFC publications  
168 (Zhang et al., 2010). Since the oxidation of toluene was achieved in the absence of an electron acceptor  
169 other than the anode, this discovery allowed them to ascertain that electrodes can stimulate the  
170 degradation of aromatic hydrocarbons in contaminated anaerobic sediments. In the same study,  
171 naphtalene was completely degraded after only 9 days in comparison to zero removal in the heat treated  
172 abiotic control and in the open circuit (OC) control. As depicted in Figure 1, research on biocatalyzed  
173 remediation in MFCs only accelerated in 2014. Mohan & Chandrasekhar (2011) found further evidence  
174 of PAH removal in BESs: they observed that a soil MFC was capable of easily attacking 5-6 ring  
175 aromatics within petroleum sludge while anaerobic degradation was only restricted to 2-3 ring aromatics  
176 (Venkata Mohan and Chandrasekhar, 2011). Since then, within six years, only about 23 publications  
177 (Table 1) focus on the potentials of PAH remediation within bioelectrochemical systems, first and  
178 foremost from TPH contaminated soil, diesel and engine oil which contain hydrocarbon mixtures of  
179 alkanes, aromatic hydrocarbons and resin-asphaltenes as sole carbon sources. In these studies, co-  
180 substrates were never used except for one study in which electricity generation and PAH degradation  
181 were improved after glucose addition to a saline soil MFC (Li et al., 2016a).

### 182 *Range of PAH concentrations, experiment duration, working volumes, voltages and current* 183 *densities*

184 Initial hydrocarbon concentrations in soil, sediment, domestic wastewater and synthetic media range  
185 from 8 mg to 12 g/kg of dry soil, 2-10 mg/kg of dry matter of sediment and 0.02 g to 30 g/L in aqueous  
186 media (Table 1). The studies employ single aromatic hydrocarbons such as naphtalene, anthracene,

187 phenanthrene and pyrene for spiking but also contaminants from polluted sites such as total petroleum  
188 hydrocarbons, engine oil or diesel. All experiments were achieved under batch or fed-batch regime  
189 within MFCs. Experiment duration can vary between 17 and 376 days while reactor working volumes  
190 range between laboratory scale (100-500 ml) and pilot scale (10-50 L) experiments. The potentials that  
191 were measured across external resistors between 100 and 1000  $\Omega$  range from 16 to 366 mV. Highest  
192 current and power densities, respectively, among all MFCs that processed hydrocarbons attained 299  
193  $\text{mA/m}^2$  (Li et al., 2016b) in rather dry conditions, reaching as high as 198  $\text{mA/m}^2$  (21  $\text{mW/m}^2$ ) in watery  
194 media (Chandrasekhar and Venkata Mohan, 2012). An exceptionally strong current density of 6  $\text{A/m}^2$   
195 was reported in a soil MFC (Zhou et al., 2016) as described further in chapter 4, section “Anode surface &  
196 buildup”.  
197

#### 198 *Differences in the performances of PAH-degrading MFCs in solution, sediment and soil*

199 The removal of PAHs is generally high in liquid media, often reaching 100 % when a minimal media  
200 (Adelaja et al., 2015, 2014) were used. It varied between 55 and 82 % for PAH-containing liquids such as  
201 real-field petrochemical wastewater (Yeruva et al., 2015), waste engine oil from saline water (Sabina et  
202 al., 2014) or diesel-contaminated media (Morris et al., 2009). In wastewater, the highest removal rate of  
203 an aromatic fraction in MFC in aqueous media reached 70 % within 17 days with an initial load of 3 g  
204 TPH/L. As for sediment, the first study that employed electrodes for increasing bioremediation in  
205 sediments achieved 24 % removal of a petroleum hydrocarbon mixture. This was a 12 fold improvement  
206 compared to the natural attenuation of the compounds (Morris and Jin, 2012). The highest removal for  
207 sediment microbial fuel cells (SMFCs) was 95 to 99 % for phenanthrene and pyrene, respectively, when  
208 BES treatment was combined with a ferrihydroxide addition (Yan et al., 2012). However it was suspected  
209 that biodegradation in SMFCs might depend on the polarity of the contaminant. In comparison to the  
210 control, more polar hydrocarbons such as alcohols and carboxylic acids were better removed in a SMFC  
211 than non-polar compounds like PAHs and nitrogen or sulfur containing cyclo- hexanes and -pentanes (Xia  
212 et al., 2015). In soil, degradation efficiencies of MFCs were generally lower (maximal 53 % at an initial  
213 load of 30 g/L). Supposedly this is because soil has a 90 % lower water content than sediment (soil water  
214 content is usually less than 60 %) (Wang et al., 2012).

## 215 **4. Configuration of microbial bioelectrochemical systems for polycyclic aromatic** 216 **hydrocarbon removal**

### 217 *Anode surface & buildup*

218 Zhou et al. recently explored the electricity producing capacity of petroleum hydrocarbon degraders in  
219 soil that were isolated from the same soil (Zhou et al., 2016). They observed current and power densities  
220 reaching 6  $\text{A/m}^2$  (220  $\text{mW/m}^2$ ). These values are much higher than previously reported and are  
221 attributed to the larger electrode surface of the carbon cloth (Lu et al., 2014a, 2014b). The  
222 corresponding degradation results have not yet been reported. Other authors have determined that  
223 bioelectrochemical remediation of petroleum hydrocarbons in soil can be achieved beyond a certain  
224 distance using a multi-anode configuration which is designed to increase the anode surface. This resulted  
225 in higher degradation rates of 18 % (TPH), 36 % (PAH) and 29 % (n-alkanes) compared to natural  
226 attenuation (Li et al., 2014). As an example, net concentrations of phenanthrene in all soil layers (1-5 cm



227 from the air-cathode) decreased below 1000 ng/g dry soil while natural attenuation showed a lower  
228 performance with a remaining phenanthrene concentration above 1500 ng/g dry soil (data from figure).  
229 The TPH removal within a distance of 5 cm from the electrode was explained by an enhanced collection  
230 of electrons in the vicinity of each anode layer (Li et al., 2014). At present, the use of multi-anodes has  
231 resulted in a seven fold higher accumulation of charge compared to a corresponding single anode setup.  
232 A possible up-scale for field applications was proposed by Lu et al. who used a pilot scale MFC of 50 L  
233 with biochar and graphite granules as anode material (Lu et al., 2014b). TPH biodegradation was  
234 improved by 241 % with respect to the control. In the column-type reactor, TPH removal extended to the  
235 sides of the reactor, producing an 82 to 90 % efficiency within an operating radius of 34 cm. Another  
236 bioelectrochemical build-up that accelerated the biodegradation of petroleum hydrocarbons in sediment  
237 involved a simple conductive graphite rod that was used to connect the anoxic sediment with the  
238 overlying oxic water in order to provide the bacteria with oxygen (Cruz Viggi et al., 2015). Oxygen, as a  
239 high redox potential electron acceptor, should consequently accelerate oxidative biodegradation.  
240 Indeed, after 200 days, biodegradation of petroleum hydrocarbons led to a 12 % and 21 % removal with  
241 one or three graphite rods, respectively, whereas only a small removal rate was observed for the biotic  
242 control without graphite..

#### 243 *Anaerobic versus aerobic cathode (MEC versus MFC)*

244 To our knowledge, only two publications concerning PAH removal in a BES with an anaerobic cathode  
245 (MEC) are available. The first study used an anaerobic cathode for the bioremediation of naphthalene  
246 (100 $\mu$ M) in a dual chamber BES where both electrode chambers were flushed with a mixture of nitrogen  
247 and carbon dioxide (95/5) to maintain anaerobic conditions (Zhang et al., 2010). Naphtalene was  
248 completely removed after only 9 days while the sterile and open circuit controls did not show any  
249 removal. This outcome was the first evidence that an electrode as electron acceptor can stimulate the  
250 anaerobic oxidation of aromatic hydrocarbons in contaminated sediments. In the second study,  
251 Sherafatmand and Ng tested the action of a SMFC on naphthalene, acenaphtene and phenanthrene  
252 removal with either an aerobic or an anaerobic cathode that they obtained by both diffusing air in the  
253 overlying water column of the SMFC or by sealing the reactor (Sherafatmand and Ng, 2015).  
254 Interestingly, results for the anaerobic cathode removal were much higher for two of the PAHs (76.9 %  
255 naphthalene, 52.5 % acenaphtene, 36.8 % phenanthrene) than results for the degradation with an  
256 aerobic cathode (41.7 % naphtalene, 31.4 % acenaphtene, 36.2 % phenanthrene). Nevertheless, both  
257 treatments exceeded the natural attenuation of all PAHs, some by a factor of three (natural: 29 %  
258 naphtalene, 29 % acenaphtene, 12 % phenanthrene). The authors stipulated that the potential  
259 difference between anode and cathode led to a change in the physical and chemical properties of soil  
260 that consequently stimulated the prevailing microorganisms. These pioneering studies exemplify that  
261 there is a significant opportunity to biodegrade PAHs in BESs where oxygen is completely absent from  
262 both electrode chambers.

#### 263 *Redox contrasting microenvironments*

264 As already discussed in this chapter, PAHs can be degraded under various redox conditions. Yan et al.  
265 combined the addition of ferric hydroxide with the treatment of PAHs in a SMFC (Yan et al., 2012). The  
266 addition of electrodes under ferric conditions was found to enhance phenanthrene and pyrene  
267 degradation rates more than twofold. A 99.5 % phenanthrene removal was achieved after 240 days in



268 comparison to Fe(III) addition alone (87.6 %) and natural attenuation (80.3 %). The combined use,  
269 testified for accelerated humic acid consumption and final sequestration of PAHs to less bio-available  
270 fractions of the sediment with removal efficiencies of phenanthrene and pyrene reaching 99.5 % and  
271 94.8 % respectively. Lastly, the combined treatment of macrophyte plantations and the use of a SMFC  
272 accelerated the biodegradation rates of benzo(a)pyrene and pyrene by about 70 % in comparison with  
273 separate macrophyte and SMFC treatments(Yan et al., 2015). The SMFC enabled the development of  
274 anoxic zones in the sediment, thereby increasing the number of aerobic as well as anaerobic PAH  
275 degraders. The creation of redox contrasting environments most probably enhanced the syntrophic  
276 metabolism between aerobic and anaerobic microbial communities for a successful removal of higher  
277 weight PAHs.

## 278 **5. Impact of environmental parameters on polycyclic aromatic hydrocarbon** 279 **removal in microbial bioelectrochemical systems**

### 280 *Conductivity*

281 Hydrocarbon degrading MFC in soil was optimal both in terms of current density (299 mA/m<sup>2</sup>) and  
282 remediation efficiency (484 % higher degradation rate than the control) when carbon fibre was added  
283 after having rinsed saline soil with distilled water (Li et al., 2016b). Accordingly, net PAH removal in the  
284 connected MFCs ranged between 44 and 88 %. While 1-3 ring PAHs were removed very efficiently the  
285 concentration of 4-6 ring PAHs also decreased. This bioremediation success resulted from electron  
286 transfer promotion and current collection by the conductive carbon material. The soil electrical  
287 conductivity of the control MFC without carbon fibre addition was 0.61 mS/cm whereas the carbon fibre  
288 supplemented soil MFC showed a 2.5 fold higher electrical conductivity of 1.5 mS/cm. The corresponding  
289 open circuit controls had 110 % and 419 % lower conductivities. In this study, the authors correlated  
290 strong degradation rates of hydrocarbons with stronger naphthalene dioxygenase and xylene  
291 monooxygenase activities in comparison relative to the non-carbon fibre control. Interestingly, even the  
292 high molecular weight fractions of hydrocarbons (C<sub>28</sub>-C<sub>36</sub>, 4-6 ring aromatics) could be degraded in this  
293 MFC. Moreover, the easy recovery of the carbon fibre could allow for its reuse. As a comparison, the soil  
294 conductivity of another saline soil MFC that processed petroleum hydrocarbons ranged between 7 and  
295 14 mS/cm. The MFC with the highest water content (33 %) and highest conductivity achieved a 120 %  
296 higher TPH degradation rate than the open circuit control (Wang et al., 2012). A comparison between  
297 conductivities indicates that even though conductivity appears to enhance microbial electron transfer  
298 reactions, the measurement of conductivity alone cannot be a sufficient indicator of removal success.  
299 For example, salts such as sodium chloride can cause microbial inhibition in spite of enhanced soil  
300 conductivity. On the contrary, conductive materials such as carbon fibre act as electron transport  
301 promoters without inhibiting microbial metabolisms. Interspecies electron transfer (IET) via electric  
302 currents through carbon materials and other conductors exhibits faster electron transfer mechanisms  
303 compared to interspecies hydrogen transfer (Cruz Viggi et al., 2014) and could therefore explain  
304 enhanced bioremediation of PAHs. As another example, the addition of 1 % (w/w) carbon fibre to a soil  
305 MFC could further enhance PAH removal compared with the MFC without carbon fibre. In open circuit  
306 controls without carbon fibre, the net concentration of 16 PAHs decreased by 5% whereas the equivalent

307 closed circuits showed a 5 fold removal. However, the carbon fibre MFC outcompeted the classic MFC  
308 with a 7.5 times higher removal rate than in the open circuit (Li et al., 2016c). Interestingly, the open  
309 circuit control containing carbon fibre similarly outcompeted the open circuit control without carbon  
310 fibre. This confirms that the sole presence of carbon fibre can enhance PAH removal even if electrodes  
311 are not connected. Likewise, semi-conductive minerals (Kato et al., 2012) as well as granular activated  
312 carbon have boosted methane production through improved IET when added to anaerobic digestors (Liu  
313 et al., 2012). This explains why conductive carbon materials such as activated carbon of different sizes (S.  
314 Xu et al., 2015) , biochar (Chen et al., 2014a) and carbon cloth (Chen et al., 2014b) have been proposed  
315 as a tool for accelerated electron transfers between species.

### 316 *Correlation between power density and polycyclic aromatic hydrocarbon removal*

317 The relationship between the power density of a MFC and biodegradation efficiency has been poorly  
318 investigated. However, a correlation between current or power density and the degree of PAH  
319 biodegradation inside BESs could be an easy approach for monitoring *in situ* PAH removal issues. In  
320 certain electrokinetic studies, the degradation of diesel (Mena et al., 2014) and petroleum hydrocarbons  
321 (T. Li et al., 2010) was found to increase as the current intensity rose. Petroleum was mixed to soil at a  
322 level of 50 g/kg dry soil and an electric current was constantly supplied at a voltage of 1 V/cm. There are  
323 two reasons for the accelerated removal of petroleum hydrocarbons: in general the supplied current  
324 supports microbial activity; but more particularly it can boost the metabolism of HDB that use oil as a  
325 sole carbon substrate. MECs are also equipped with a small current that is applied to the existing  
326 microbial community. Until present, only a few studies on the above-mentioned anaerobic cathodes  
327 (MEC setups) are available in the literature. Nevertheless, the suggestion that the removal of  
328 hydrocarbons can be improved with the assistance of an anode in MFCs is supported by the close  
329 relationship between charge output, the presence of HDB and PAH removal. Various studies show an  
330 increase in the number of HDB in soil close to the anode (1cm). Wang et al. tested anodes that were  
331 precultured with exoelectrogenic bacteria for TPH removal in petroleum in contaminated soil (Wang et  
332 al., 2012). As a result, the number of HDB within 1 cm from the anode increased by almost two orders of  
333 magnitude, rising from  $8 \cdot 10^3$  CFU/g-soil to  $373 \cdot 10^3$  CFU/g-soil in comparison with the open circuit  
334 control. Consequently, the net biodegradation of 16 PAHs increased from 30 to 42 % within 25 days  
335 when the soil MFC had a water content of 33 %. The substantial increase in the amount of HDB highlights  
336 the biostimulation of their growth by the colonisation of exoelectrogenic bacteria in the same system.  
337 The authors stipulated that the limited biostimulation beyond a certain distance from the anode results  
338 from the need for exoelectrogenic bacteria to connect to the anode either through direct contact or  
339 through a conductive network which is limited in length (Wang et al., 2012). The study that testified the  
340 highest current density (299 mA/m<sup>2</sup>) also reported, after 65 days, the strongest removal rate with a 153  
341 to 484 % higher TPH degradation rate relative to the control. Nevertheless, other authors did not find  
342 any correlation between power densities and biodegradation rates; they have attributed this  
343 observation to oxygen intrusion (Adelaja et al., 2015), substrate to biomass conversion (Hu et al., 2011)  
344 and electron losses due to electron transfer from substrates to other electron acceptors such as sulfates  
345 in solution and/or assimilation of electrons for bacterial growth (Liu et al., 2005).

### 346 *Porosity & mass transfer*

347 The addition of sand was found to increase the soil porosity inside bioelectrochemical reactors; this  
348 probably enhanced PAH transfer simultaneously with a general improvement in mass transfer (Li et al.,  
349 2015). The authors pointed to a reduced ohmic resistance (by 46 %) in such a way that petroleum  
350 hydrocarbon removal was improved by 84 % within 135 days compared to the control MFC without any  
351 sand supplement. In particular, the degradation of n-alkanes and PAHs with high molecular weights was  
352 accelerated. However, the enhanced porosity of the soil also enabled more oxygen diffusion into the soil  
353 layers thus suggesting the possibility that some PAH degradation may be due to aerobic processes. The  
354 enrichment of the species *Alkanivorax* in the layer closest to the cathode supposedly accounts for the  
355 biodegradation of petroleum hydrocarbons. In addition, *Geobacteraceae* species were detected  
356 according to the supposed exoelectrogenic activity in this layer. Another approach to improve mass  
357 transfer for enhanced TPH degradation in soil was proposed by Zhang et al. The group compared  
358 hydrocarbon degrading MFCs (contaminated soil from real-field) with a horizontal (HA) and a vertical  
359 arrangement (VA) of anodes. A lower resistance of mass transport in the HA than that of the VA seemed  
360 to result in increased power generation and more TPH degradation (Zhang et al., 2015).

### 361 *Salinity*

362 Since 40 % of the worlds' soils are saline environments, Serrano and Gaxiola (1994) decided to  
363 investigate the effect of salinity on PAH removal in BES. They found that the performance of a  
364 hydrocarbon degrading saline soil MFC could be enhanced by rinsing the saline soil with distilled water.  
365 This rise in microbial activity was achieved following the reduction in salinity that was initially causing  
366 inhibition (Li et al., 2016b). Before rinsing, the soluble salt content was 8.6 times higher than after rinsing  
367 (2.8 % compared to 0.3 %). Optimum conditions for soil MFCs included a 1 % salt content (w/v) for which  
368 91.6 % and 79.1 % of hydrocarbons and COD, respectively, were removed, with a maximum power  
369 density of 1.06 mW/m<sup>2</sup> (Adelaja et al., 2015). Furthermore, waste engine oil was used as an organic  
370 substrate in a desalination microbial fuel cell that achieved biodegradation of branched and cyclic  
371 aliphatic hydrocarbons (70.1 ± 0.5 %) along with desalination (68.3 %) and power production (3.1  
372 mW/m<sup>2</sup>) (Sabina et al., 2014). In consequence, 8 % more hydrocarbon was removed than when  
373 preliminary flask studies were carried out with the same *Bacillus subtilis* moh3 culture isolated from  
374 waste engine oil.

### 375 *Sorption of polycyclic aromatic hydrocarbons on soil and on electrodes*

376 Since PAHs are hydrophobic contaminants, they tend to adsorb equally to hydrophobic surfaces. An  
377 observed removal can be related either to the biodegradation of a contaminant, to its sequestration to  
378 organic matter (Yan et al., 2012) or to adsorption to the electrode of a MFC as demonstrated for benzoic  
379 (Yang et al., 2013) and trace organic compounds (Wang et al., 2015). Indeed, adsorption controls should  
380 be performed so that the actual remains of an environmental pollutant inside a matrix or its  
381 decomposition to a metabolite can be distinguished. For instance, adsorption controls have revealed  
382 that the carbon anode of a MFC exhibits a high affinity for phenanthrene with a maximum adsorption  
383 capacity of 0.45 mg/cm<sup>2</sup> (Adelaja et al., 2015). Yet, sterile adsorption controls in order to monitor the  
384 abiotic physical parameters have not been performed systematically throughout all studies.

385 An exemplary study determined the degradation efficiencies and rates of petroleum hydrocarbons based  
386 on their remains in solution and on hydrocarbons adsorbed to the electrode at the end of a MFC  
387 operation (Adelaja et al., 2015). Phenanthrene concentrations in the bulk solution rapidly decreased by  
388 90 % within 24 hours, eventually reaching more than 95 % in all fed-batch cycles after 60 days. This fast  
389 decrease was attributed to the disappearance of phenanthrene from solution by adsorption to the  
390 electrode; microbial degradation of the compound then accounts for the subsequent gradual decrease. It  
391 has been previously reported that microorganisms can degrade aromatic hydrocarbons on an electrode  
392 and in solution; however, the hydrocarbons need to be initially adsorbed (Zhang et al., 2010). This point  
393 of view has already been described by Lovley et al. who stated that electrodes co-localise  
394 micropollutants and electrophilic microbes at the site where degradation finally takes place (Lovley,  
395 2006). Therefore, PAHs may desorb from the electrode then follow a biodegradation process which may  
396 occur directly on the electrode. Both processes might also take place concomitantly. At present the  
397 underlying mechanisms are not at all clear. Chandrasekhar and Venkata Mohan (2012) hypothesized that  
398 the oxidation of lower aromatic compounds at the anode could result in OH<sup>-</sup>-radicals that might attack  
399 higher ring structures. In their view, aromatic hydrocarbons adsorbed to the anode surface can serve as  
400 a source of carbon for microorganisms

401 The above-mentioned hypotheses strongly depend on the electrode material. Two studies on the  
402 bioavailability of phenanthrene adsorbed to black carbon (BC) without application of a current both  
403 showed different results. In the first study, the addition of BC to soil led to a significant reduction in  
404 microbial mineralization of phenanthrene (Rhodes et al., 2008); in the second, microbes could utilize  
405 about 84 % of phenanthrene adsorbed to BC after aging for 21 days (Xia et al., 2010).

#### 406 *Desorption of polycyclic aromatic hydrocarbons by surfactant addition*

407 Interestingly, surfactant (Triton x-100) addition to a soil MFC equipped with a carbon cloth anode led to a  
408 negative impact on the electricity production and TPH removal (Lu et al., 2014a). These authors assumed  
409 that accessibility of TPH for bioelectrochemical and microbial degradation in the aqueous phase was  
410 reduced when the surfactant sorption to soil at a surfactant concentration of 500 mg/L increased. They  
411 suggested that the soil-surfactant-sorption also resulted in increased TPH partitioning onto soil particles.  
412 On the contrary, Alcántara et al. and Gomez et al. demonstrated that PAH removal could be enhanced by  
413 surfactant addition (Tween 80) to soil. 80 to 85 % of fluoranthene, benzo(a)anthracene and pyrene were  
414 desorbed from a soil matrix into the aqueous phase and subsequently electrochemically degraded  
415 (Gómez et al., 2010). In a similar experimental setup 86 % phenanthrene was desorbed from soil after  
416 ten days and 96 % was removed with the application of a 5 V tension for 3 days (Alcántara et al., 2009).  
417 Given these contradictory results, the right combination between soil, surfactant and PAHs still needs to  
418 be determined so PAHs may be desorbed from soil or sediment and so biodegradation within BESs can  
419 be enhanced.

## 420 6. Microbial insights on polycyclic aromatic hydrocarbon removal in microbial 421 bioelectrochemical systems

### 422 *Syntrophy*

423 Electroactive species can be found in diverse habitats and are affiliated to many different  
424 microorganisms such as *Clostridia*, *Bacilli* and different *Proteobacteria*, thus pointing to the absence of  
425 an ecological niche for exoelectrogens (Koch et al., 2014). In addition, the complex nature of organic  
426 waste requires a diverse microbial community for disassembling its chemical components (Logan and  
427 Rabaey, 2012), thus giving rise to syntrophic degraders. The positive effect of electricity in PAH  
428 bioremediation is probably related to bioelectrochemical catalysis in which HDB are favoured by the  
429 presence of electroactive microorganisms. A syntrophic relationship between exoelectrogens and  
430 various bacterial phyla has already been determined by various scientists (Kiely et al., 2011; Kimura and  
431 Okabe, 2013; Lu et al., 2012). Fermentative bacteria and acetate consuming anode respiring bacteria  
432 (Parameswaran et al., 2009) as well as methanogenic communities and exoelectrogens (Rotaru et al.,  
433 2014) have been observed to interact on the basis of cooperative metabolite production and  
434 consumption. This is no surprise since syntrophic bacteria drive the anaerobic degradation of certain  
435 fermentation products (e.g., butyrate, ethanol, propionate) into intermediary substrates (e.g., H<sub>2</sub>,  
436 formate, acetate) (Schmidt et al., 2016) that can eventually be used by exoelectrogens and/or  
437 methanogens. Although a syntrophic relationship between HDB and an exoelectrogen has not yet been  
438 proven, a metabolic cooperation could be imagined between heterotrophs in soil from the  $\alpha$ - or  $\beta$ -  
439 *Proteobacteria* phylum such as *Sphingomonas* or *Burkholderia* genus. These organisms use diverse  
440 substrates among other recalcitrant aromatic and phenolic compounds as carbon sources (Aislabie et al.,  
441 2013). Interestingly, *Burkholderia cenocepacia* was identified as the microorganism that produced the  
442 oxidant for exoelectrogens in a MFC (Hunter and Manter, 2011). *Burkholderia* species were also  
443 acknowledged as one of the dominant members of an anode chamber microbial community in a MFC  
444 using acetate as anodic substrate (Quan et al., 2012). The results described in chapter 5, section  
445 “Correlation between power density and polycyclic aromatic hydrocarbon removal” suggest that  
446 electricity generating bacteria enhance HDB activity (Zhang et al., 2012) through a syntrophic  
447 metabolism, namely by accepting additional electrons from the metabolites of HDB degradation. By  
448 shuttling them to the anode, they supposedly alleviate thermodynamic limitations of PAH removal  
449 similar to those described under methanogenic conditions (Christensen et al., 2004) when *Archaea*  
450 consume hydrogen to keep hydrogen partial pressure low enough for an exergonic reaction to occur  
451 (Gieg et al., 2014). Furthermore, microbial community analysis from an olive mill wastewater treating  
452 MFC has shown that both exoelectrogenic and phenol-degrading microorganisms from the  
453 *Sphingomonas* phylum were concentrated in the anode biofilm (Bermek et al., 2014).

### 454 *Promising microbes for PAH removal in BESs*

455 Several studies cite the *Proteobacteria*, *Firmicutes* and *Bacteroidetes* phyla comprising bacteria  
456 belonging to the *Enterobacteriaceae* and *Pseudomonadaceae* families that could be potential key players  
457 of PAH removal in BESs. Likewise, *Escherichia* species (Li et al., 2014; Lu et al., 2014a) and the *Gamma*-  
458 and *Delta-Proteobacteria* as well as *Negativicutes* and *Bacilli* (*Firmicutes*) classes are possible candidates  
459 for successful PAH biodegradation in MFCs (Table 2) since their abundances have shown positive

460 correlations with hydrocarbon degradation (Li et al., 2016a; Venkidusamy et al., 2016). Differences in  
461 functional bacteria can be observed for crude oil and diesel degradation. Accordingly, 71 % of the  
462 predominant  $\gamma$ -Proteobacteria in a crude oil degrading MFC were *Escherichia sp.* (Li et al., 2016a)  
463 whereas the dominant phylum following bioremediation of diesel contaminated soil was  $\beta$ -  
464 *Proteobacteria* including mainly genera of *Achromobacter*, *Alcaligenes*, *Bordetella*, *Comamonas*, and  
465 *Pusillimonas* (Lu et al., 2014a). As an example for microbial selection during bioelectrochemical  
466 treatment, the abundance of *Firmicutes* increased by 346 % on average during the BES-treatment of a  
467 petroleum contaminated soil, at a much higher degree than for conventional bioremediation (Popp et  
468 al., 2006). Furthermore, a study by Lu et al., pointed out that all exoelectrogens belonged to  
469 *Proteobacteria*. More specifically, exoelectrogens that could also degrade hydrocarbons belong to the  
470 *Enterobacter* and *Pseudomonas* genera. The recognised hydrocarbon degraders and exoelectrogenic  
471 bacteria *Pseudomonas putida* and *Pseudomonas aeruginosa* were also part of the anode biofilm.  
472 *Pseudomonas* species respire anaerobically via the production of phenazines and pyocyanin. These  
473 electron shuttling compounds can in turn help microbial co-oxidation of contaminants such as  
474 phenanthrene via electron transfer to the anode (Qiao et al., 2015). In addition, Venkidusamy et al.  
475 reported sequence similarities with *Geobacillus* and *Megasphaera* species that both participate in  
476 current generation of mediator-less MFCs and diesel degradation (Liu et al., 2009; Venkidusamy et al.,  
477 2016). The anode biofilm of another diesel degrading MFC contained *Shewanella* and *Dechloromonas*  
478 species. Certain *Dechloromonas* species such as *Dechloromonas aromatica* are capable of degrading  
479 aromatics, (Salinero et al., 2009). They can use toluene, benzene and xylene as electron donors under  
480 anaerobic conditions coupled to nitrate reduction (Chakraborty et al., 2005). The discovery of the  
481 *Shewanella* species is promising since *Shewanella oneidensis* and *Shewanella putrefaciens* are part of  
482 many MFC anode biofilms (Gorby et al., 2009). Moreover, *Shewanella* species have been found to  
483 possess nanowires which are believed to improve the utilization of the anode as an electron acceptor  
484 (Gorby et al., 2009).

#### 485 *An excellent microbe for PAH removal in BESs: Geobacter?*

486 Disregarding the fact that high power densities from complex sources of organic matter are typically  
487 associated with the presence of *Geobacteraceae* in the anodic community (Kiely et al., 2011), *Geobacter*  
488 *metallireducens* (Zhang et al., 2013) and *Geobacter sulfurreducens* (Zhou et al., 2016), in particular, can  
489 initiate the degradation of benzene and naphthalene respectively. Beside their capacity of mediated and  
490 unmediated electron exchange using self-produced flavins (Park et al., 2016; TerAvest and Angenent,  
491 2014), they have also been found to facilitate substrate degradation and power production in MFCs  
492 through nanowires (Bond and Lovley, 2003; Shu et al., 2016). The pilin proteins potentially enable direct  
493 electron exchange with co-cultured species, as seen for a co-culture of *G. metallireducens* and the  
494 methanogen *Methanosarcina barkeri* (Cheng and Call, 2016) as well as direct interaction with an  
495 electrode (Ding et al., 2016; Malvankar and Lovley, 2014). *Geobacteraceae* have been found in two  
496 petroleum removing MFCs (Li et al., 2014; Zhou et al., 2016) and one toluene removing MEC (Zhang et  
497 al., 2010), thus representing three out of nine publications that investigated the presence of specific  
498 microbial phyla in PAH degrading BESs (Table 2). Interestingly, the capacity of a soil-MFC to selectively  
499 enrich exoelectrogenic hydrocarbon degraders was convincingly demonstrated by the isolation of two



500 exoelectrogens from *Geobacter* and *Ochrobactrum* species that used petroleum hydrocarbons as a sole  
501 carbon source (Zhou et al., 2016).

## 502 **7. Perspectives for polycyclic aromatic hydrocarbon removal in microbial** 503 **bioelectrochemical systems**

### 504 *Enrichment cultures for PAH bioremediation in BESs*

505 Correlation analysis testified that the biodiversity in soil beyond a certain distance from the cathode was  
506 mainly determined by the concentration of petroleum hydrocarbons, while the biodiversity in soil close  
507 to the cathode was dominated by the current (Li et al., 2016a). The change in microbial community  
508 structure in hydrocarbon-degrading MFCs in comparison to their open circuit controls clearly  
509 demonstrated that BESs significantly impact the metabolic pathways of biota present in soil or sediment.  
510 BESs assumedly favour syntrophic cooperation between different phyla of microorganisms such as  
511 *Geobacter* and *Ochrobactrum*. Studies with enrichment cultures that employ both known PAH degraders  
512 as well as exoelectrogens should be encouraged to advance our knowledge on the syntrophic  
513 relationships between them, to determine how PAH removal can be improved in these systems and to  
514 apply acquired knowledge to *in situ* experiments.

### 515 *Conductive materials for PAH bioremediation in BESs*

516 The more conductive carbon materials have proved to enhance PAH removal in MFCs (Li et al., 2016b,  
517 2016c) and to improve IET in anaerobic digestion (Liu et al., 2012). Nevertheless, the detailed  
518 mechanisms explaining how these materials contribute to the observed performances still have to be  
519 determined (Kouzuma et al., 2015). To shed light on this matter, experiments investigating the  
520 relationship between soil conductivity, the addition of conductive materials and the biostimulation  
521 success of PAHs by BESs should be encouraged. A second unknown factor is the relationship between the  
522 supplied current and degradation efficiency of PAHs in MECs. However, a positive correlation between  
523 the biodegradation of PAHs and the amount of supplied current has been demonstrated in several  
524 electrokinetic studies (T. Li et al., 2010; Mena et al., 2014). Examples of positive correlations between  
525 current density and PAH biodegradation in MFCs have been put forward although, it is yet unclear  
526 whether the success of bioremediation through the application of current in MECs is due to a change in  
527 soil properties or whether the metabolism of HDBs is accelerated more directly. There is still a need for  
528 further research to be conducted in order to verify these hypotheses.

### 529 *Anaerobic cathodes for PAH bioremediation*

530 To our knowledge, few published studies have investigated the use of anaerobic cathodes to remove  
531 PAHs inside BESs, and none have yet attempted the use of biocathodes. Nonetheless, the few existing  
532 studies all point to opportunities for successfully removing PAHs, as discussed in chapter 4, section  
533 “Anaerobic versus aerobic cathode”. Further studies are still required using anaerobic cathodes in order  
534 to answer the question whether MECs can be as efficient for PAH removal as MFC setups.  
535 Bioremediation in MECs could become an auspicious technology for treating contaminants in strictly  
536 anaerobic aqueous or solid media. For instance, Liang et al. degraded the chloramphenicol antibiotic  
537 (CAP) in a MEC in which denitrification and dechlorination of the compound took place in the biocathode



538 chamber. The MEC attained removal efficiencies of 96 %, a result which is 20 % higher than CAP removal  
539 in the control experiment with an abiotic cathode (Liang et al., 2013). In aqueous media it could be  
540 possible to use a single cell containing a bioanode and biocathode in the same compartment. This would  
541 favour sequential redox-reactions of PAHs where ring fission could be followed by further decomposition  
542 of alkylchains. However, knowledge concerning the microbial key players of anaerobic biocathodes in  
543 MECs is still sparse (Jafary et al., 2015; Parkhey and Gupta, 2017). Biocathodes in MECs are most often  
544 only employed for enhancing hydrogen production (Kadier et al., 2016; Lu and Ren, 2016), therefore it is  
545 crucial that research on PAH bioremediation in MECs should be initiated.

#### 546 *Conventional versus bioelectrochemical PAH bioremediation*

547 Bioelectrochemical remediation of contaminated soil, sludge and sediment can be an inexpensive  
548 alternative to conventional *in situ* bioremediation. Currently, certain authors rather consider the  
549 performance of MFC technology for waste or wastewater treatment than for the generation of high  
550 current densities (Li and Yu, 2015; Zhang et al., 2016). The low but stable electricity gain of SMFCs could  
551 be used to power biosensors that monitor the on-site state of pollution during real time operations. For  
552 instance, King et al. proved the utility of MFCs as biosensors for the detection of recalcitrant organics  
553 such as bisphenol A in water (King et al., 2014). Not least, the use of SMFCs as long term electrical power  
554 sources for sensors and buoys has been confirmed (Tender et al., 2008). Indeed, with the help of a SMFC,  
555 Yang et al. charged batteries for electrical devices such as a camera and mobile phone (Yang et al., 2015).  
556 Moreover, in cases where *in situ* bioremediation would require a small voltage, solar energy could be  
557 collected by placing a biocathode at the subsurface of a polluted site, thus benefitting from the  
558 advantage of low maintenance costs (Lovley, 2011).

#### 559 *Scaling of bioelectrochemical systems for PAH bioremediation*

560 Most MFC studies, for the removal of both organic pollutants and COD, are still limited to laboratory or  
561 pilot-scale experiments. Problems arise at these scales with low power output owing to ohmic losses  
562 (Cusick et al., 2011) and unfavourable biomass production in continuous flow operations (Logan, 2010).  
563 For this reason, field experiments on hydrocarbon removal from contaminated sites should be  
564 encouraged in order to validate *in situ* applications, especially when authors are confident towards large  
565 field implementations without loss of removal efficiency (Lu et al., 2014b). When aiming at large scale  
566 applications for recalcitrant pollutant treatments with BESs, it would be preferable to focus research  
567 efforts on the study of PAH treatment with mixed cultures. These would be more robust when adapted  
568 to changing microenvironments and less susceptible to contaminations. This demand for real-field up-  
569 scaling goes hand in hand with the need for lab-scale studies during which experimental parameters can  
570 be better controlled and treatment efficiencies are comparable between experiments. Particularly, the  
571 question whether contaminants are adsorbed or degraded after sorption to the electrode material  
572 and/or the polluted soil should be critically examined with the help of sorption controls. Simultaneously,  
573 as there are knowledge gaps in the capacity to control the microbiology of such systems, there is a clear  
574 need for fundamental research on pure or simplified culture media. This would contribute to the future  
575 engineering of site-specific processes, and to a better understanding of the electron transfer  
576 mechanisms between microbes and the surface of electrodes.

## 577 8. Conclusion

578 This review has identified the frontiers of the state of the art in PAH treatment by BESs in order to assist  
579 researchers in the field on the decisions they would have to take regarding the design of their next  
580 experimental plans in terms of configuration of the BES and of the environmental parameters that are  
581 employed. Pioneer studies conclusively demonstrate the success of the BES technology as an *in situ*  
582 approach for enhanced bioremediation of recalcitrant compounds such as PAHs, TPHs and diesel in  
583 contaminated soil, sediment and liquid media. Apparently, BESs can respond to two of the five stated  
584 limitations of PAH degradation: First and foremost, microbial bioelectrochemical systems can improve  
585 the activity of indigenous PAH degrading bacteria, thereby increasing their abundance; and secondly,  
586 they can partially circumvent the lack of PAHs in the aqueous phase by adsorbing contaminants to the  
587 surface of the electrode where they can be degraded before or after desorption. Additionally, several  
588 suggestions for further research have been put forward, taking into account the microbial aspects (e. g.  
589 culture studies with hydrocarbon degraders and exoelectrogenic bacteria) and portraying innovative  
590 methods to increase interspecies electron transfer (addition of conductive carbon materials) in BESs for  
591 an enhanced biodegradation of PAHs.

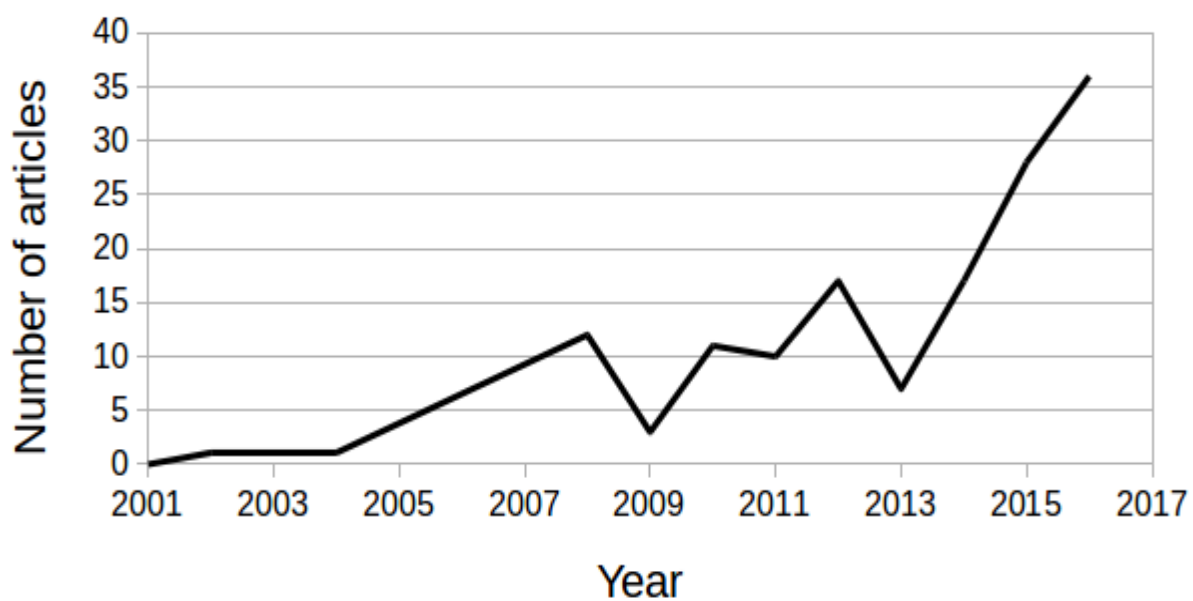
592 The main advantages of BESs for PAH bioremediation include the facts (a) that electrodes can serve as  
593 permanent terminal electron acceptors for electron discharge of biota, (b) that removal efficiencies of  
594 PAHs, TPHs and diesel can be improved without the need for a periodical replenishment of chemicals, (c)  
595 that a BES can be integrated into existing *ex situ* treatments with a potential for *in situ* treatment, (d)  
596 that the use of electrodes as electron donors and/or acceptors can generate a current for supporting  
597 electronic equipment, (e) that inexpensive and environmental friendly conductive carbon materials can  
598 be used inside BESs to further increase biodegradation and (f) that recalcitrant organic pollutants can be  
599 eliminated simultaneously with an enhanced organic matter conversion. In addition, the use of sediment  
600 or soil MFCs could alleviate the present drawbacks of *in situ* bioremediation such as expensive post-  
601 treatment for recycling or eliminating added chemicals. For this reason the use of BESs for PAH  
602 bioremediation is probably more environmentally friendly and less threatening to human health than  
603 conventional *in situ* bioremediation techniques. Albeit its challenges as a recent technology, the use of  
604 BESs for PAH biodegradation could be the way out of an impasse, since the removal of PAHs from  
605 anaerobic environments with BESs has proved to be satisfyingly diverse and efficient.

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609

## Increasing interest in MFC technology for bioremediation



610 Figure 1: Number of hits of relevant articles per year (reviews excluded) on “Web of Science” in February  
611 2017 using the key words "bioremediation" and "microbial&fuel&cell"

612

Author	Type of BES	Matrix	Pollutant	Start Concentration	Removal [%] (Degradation rate if indicated)	Controls (types and performances)	Experiment length (days)	Max. current density (CD)/ max power density (PD)* normalized by anodic or cathodic surface area
(Adelaja et al., 2014)	MFC	Synthetic medium	Benzene, phenanthrene	200 mg/L benzene, 30 mg/L phenanthrene	> 96 (for all inocula) best: mixed culture+ P. aeruginosa: 27.3 $\mu$ M/d (phenanthrene), 65.6 (COD) Others: Co-culture and pure strains (P. aeruginosa, S. oneidensis), same strains mixed with digested sludge,	For each inoculum: abiotic MFC, disconnected MFC, anaerobic control using the same inocula	60	1.25 mW/m <sup>2</sup> (normalized to the projected total surface area of the anode (40 cm <sup>2</sup> ), 18 mA/m <sup>2</sup> (data from figure), max. voltage: 65 mV (data from figure)
(Adelaja et al., 2015)	MFC	Minimal medium	Benzene, phenanthrene	100 mg/L benzene 100 mg/L phenanthrene	91.6 (benzene +phenanthrene) 79.1 (COD)	Abiotic: 20 (benzene), 10 (phenanthrene)	60	4.89 mA/m <sup>2</sup> , 0.72 mW/m <sup>2</sup>
(Chandrasekhar and Venkata Mohan, 2012).	MFC	Domestic wastewater	Real field petroleum sludge	3000, 9000, 15000, 30000 mg TPH/L sewage OL1 (3 g) OL2 (9 g) OL3 (15 g) OL4 (30 g)	58 (aromatics at 30 g TPH/L) 70 (aromatics at 3 g TPH/L)	Four organic loading (OL) conditions: Low load better for power generation, high load better for substrate degradation	17	20.6 mW/m <sup>2</sup> , 198.3 mA/m <sup>2</sup> at 3g TPH/L, 11.8 mA/m <sup>2</sup> at 30g TPH/L
(Li et al., 2016b)	SMFC	Saline Soil	TPHs, n-alkanes, PAHs	Max: 0.484 mg/kg (PAH), Max:20.181 mg/kg (n-alkanes)	153-484 % higher TPH degradation rate in all MFCs compared to CK, RM>MC>RS>CK RM: 60+-9 (TPH), OSOC: 3 (TPH), PAH removal: 59 -92, n-alkanes: 44 -88, 4-6 ring PAHs particularly removed in RM	CK: unmodified soil MFC RS: rinsed soil MFC MC: carbon fiber (2 %) + original soil MFC RM: carbon fiber (2 %) + rinsed soil MFC RMOC, RSOC, OSOC, MCOC: open circuit configurations of RM,RS, CK and MC	65	299 mA/m <sup>2</sup> (RM): 595 % higher than CK
(Li et al., 2016a)	SMFC	Saline soil	TPHs, n-alkanes, PAHs (phenanthrene,	Contaminated soil: 945 mg/kg PAHs 28.322 mg/kg	TPH: 21 (LG, Layer 1, 62 % higher removal than CK) TPH removal: LG > HG > CK > LGOC > HGOC > OC	CK: closed circuit OC: open circuit LG: soil + current + low glucose HG: soil + current + high	135	HG: 43 mW/m <sup>2</sup> , ca. 108 mA/m <sup>2</sup> (with U= 0.4 V data from figure), LG: 35 mW/m <sup>2</sup> , 79 % and 46 % higher

			fluoranthene, pyrene, Chrysene accounting for 70 % of all PAHs)	(n-alkanes), LG (low glucose 0.1 % w/v) HG (high glucose 0.5 % w/v)	PAH: 34 (LG) 44 (HG)	glucose LGOC, HGOC: open circuit controls		than that of CK, CK: 24 mW/ m <sup>2</sup>
(Li et al., 2014)	SMFC	Saline Soil	C8-C40 n-alkanes, 16 PAHs	5.653 mg/kg (total PAHs) 609 mg/kg	Max. in soil layer four: 18 (TPH), 36 (PAH), 29 (n-alkane) compared to control with natural attenuation, degradation rates depending on soil layer [SL] in distance to anodes (SL 4 > SL 1 > SL 2 > SL 3), SL4 closest to air-cathode	open circuit	180	37 mW/m <sup>2</sup> , 366 mV, 102 mA/m <sup>2</sup> on day 5
(Li et al., 2015)	MFC	Aged soil	TPHs, n-alkanes, 16 PAHs	Max: 945 mg/kg (PAH) Max: 27.891 mg/kg (n-alkane)	22 (TPHs) in high ratio sand/soil MFC, (+52 % versus LS), (+84 % HS versus CK), (+268 % HS versus OC), higher removal for PAH with sand addition	Soil only (OC); soil + current (CK); sand + soil +current: low sand/soil and high sand/soil ratio= (LS)=5:1 (HS)=2:1, 15 (less sand MFC) 12 (without sand but connected electrodes) 6 (OC)	135	0.28 mA/m <sup>2</sup> /g soil 2.76 mW/m <sup>2</sup> /g soil
(Li et al., 2016c)	MFC	Soil	16 PAHs, 30 n-alkanes	7942 ± 7476 ng/g (PAHs), 701 ± 736 µg/g (n-alkanes)	5 % (CKOC), Compared to CKOC: CK showed 5-fold removal, MC showed 7.4-fold removal, MCOC 4.4 times higher than CKOC	Original soil (OS), OS + carbon fiber (MCOS), Carbon fiber MFC (CK), OS-MFC (MC), Open circuit controls : CKOC, MCOC	144	203 mA/m <sup>2</sup> , 0.8 mW/m <sup>2</sup> , 100 Ω, Average over 144 days: 120.5 mA/m <sup>2</sup> for CK, 7.5 mA/m <sup>2</sup> for MC
(Lu et al., 2014b)	MFC	Soil	Hydrocarbons from raw diesel	12300 mg/kg dry soil	82-90 (1-34 cm radius)	68	120	70.4 mA/m <sup>2</sup>

(Lu et al., 2014a)	MFC	Soil	TPHs	11460 mg/kg dry soil	78.7 (BCA) 73.1 (CCA) 62 (CCA-S; taken from figure)	41.6 (OC of BCA) 40.7(OC of CCA) CCA-S: CCA with surfactant addition	64	85.9 mA/m <sup>2</sup> , 39.1 mW/m <sup>2</sup> (BCA) 73.0 mA/m <sup>2</sup> , 17.7 W/m <sup>2</sup> (CCA), 21.2 mA/m <sup>2</sup> , 2.9 mW/m <sup>2</sup> (CCA-S)
(Morris and Jin, 2012)	MFC	Sediment	TPHs	16000 mg/kg sediment	24 (closed circuit)	2 (open circuit)	66	190 mV, 2.2 mW/m <sup>3</sup>
(Morris et al., 2009))	MFC	Ground water	Diesel range organics (DRO) C10-C28 aliphatics	176-241 mg/L	82 (DRO) 6.9 mg DRO/(L day) (or 34.5 μmol/day)	31 (cathode removed)	21	32 mW/m <sup>2</sup> Data from figure: ~175 mA/m <sup>2</sup> average 160 mV (CD and PD calculated per cathode surface)
(Venkata Mohan and Chandra sekhar, 2011)	MFC	Soil	TPHs	2-480 mg/L soil (calculated by us: 480000 mg/kg soil)	41 (Total TPH), 98 (benzo(g,h,i)perylene), 96 (dibenzo(a,h)anthracene)	Anaerobic controls: 21 (total) 68 (Benzo(g,h,i)perylene) 56 (Dibenzo(a,h)anthracene)	17	20.62 mW/m <sup>2</sup> , 198.31 mA/m <sup>2</sup> , 104 mV
(Sabina et al., 2014)	MFC	Saline water	Waste engine oil (branched, long-chain & cyclic hydrocarbons)	1 % (v/v) (100ml/L)	70.1 in desalination MFC (gravimetric decrease in engine oil)	62.9 % (gravimetric); shake flask study with Bacillus subtilis moh3)	14	3.1 mW/m <sup>2</sup> (based on the cross-sectional area of anode)
(Sherafatmand and Ng, 2015)	SMFC/ SMEC	Sediment	PAHs, naphthalene, acenaphthene, phenanthrene	50 ppm for all three PAHs (50 mg/kg)	Anaerobic cathode: 76.9 Naphthalene, 52.5 acenaphthene, 36.8 phenanthrene	Natural attenuation: 29 (Naphthalene), 29 (acenaphthene), 12 (phenanthrene), Aerobic cathode: 41.7 (Naphthalene), 31.4 (acenaphthene), 36.2 (phenanthrene)	45	2 mW/m <sup>2</sup> in anaerobic, 5.8 mW/m <sup>2</sup> in aerobic
(Venkidusamy et al., 2016)	MFC	Synthetic medium	Diesel	800 mg/L	100 (1 year selected biofilm anode)	83 (freshly inoculated anode)	30	90.8 mW/m <sup>2</sup> , 115mA/m <sup>2</sup> normalized to cathode surface

(Cruz Viggli et al., 2015)	SMFC	sediment	Spiked crude oil (TPH)	11300-12300 mg/kg dry sediment	After 200 d: 12 (S) 21 (S3) 0 (C)	S: One graphite rod, S3: three graphite rods, C: biotic without graphite rod, B: autoclaved+ one graphite rod, B3: autoclaved+ three rods,	417	No external electrical charge input or output
(Wang et al., 2012)	MFC	Saline soil	TPHs, 16 PAHs (phenanthrene, chrysene, pyrene and phenanthrene representing 75 %)	0.5- 0.8 mg/kg soil	15.2 (TPH), 120 % higher degradation rate in CC (TPH) than OC in 1 cm distance of the anode	6.9 (open circuit), CC: closed circuit	25	0.85 mW/m <sup>2</sup>
(Xia et al., 2015).	SMFC	Sediment	PAHs, cyclohexanes, cyclopentanes	ca. 3 µg/g sediment (PAHs)	< 15 %	Mainly < 10 % (open circuit)	20 days	0.6 V 4.32 mW/m <sup>2</sup> 9.29 mA/m <sup>2</sup>
(Yan et al., 2012)	SMFC	Sediment	Phenanthrene, pyrene	10 and 5 mg/kg dry sediment for phenanthrene and pyrene	94.8 (Pyrene), 99.5 (phenanthrene) (SMFC + FeOOH); combined treatment best for all anaerobic conditions except methanogenic	Open circuit: 80.3 (phenanthrene), 74.5 (pyrene); ferric hydroxide (FeOOH): 87.6 (phenanthrene) , 79.9 (pyrene); SMFC: 96.1 (phenanthrene), 92.1 (pyrene)	240	16-17 mV, average CD not reported (average per anode surface: 170 mA)
(Yan et al., 2015)	SMFC	Sediment	Benzo(a)pyrene, pyrene	2 mg/kg dry sediment (benzo(a)pyrene), 4 mg/kg dry sediment (pyrene)	87 (Macrophyte +SMFC) Combined treatment degradation rates are 70% higher than control treatments	68 (Macrophyte alone), 56 (SMFC alone), 27 (control)	367	61 -65 mV, average CD not reported directly (average given with: 650 mA/anode surface, 17 A/m <sup>2</sup> )



(Yang et al., 2015)	SMFC	Sediment	PAHs	PAH: 1.2 mg/kg wet weight, PBDE: 178µg/kg wet weight	22.1 (TOC removal in closed circuit)	3.8 (TOC removal in open circuit)	2 years	0.4 -0.6 V
(Yeruva et al., 2015)	MFC/ MFC + anoxic cathode	wastewater	Petrochemical wastewater (BOD 5 /COD: 0.36).	9.68 kg COD/m <sup>3</sup> *day	55 (COD in anoxic SBR-BET), 49 (COD in aerobic SBR-BET) SBR: Sequential batch reactor BET: Bioelectrochemical treatment	34.6 (COD anoxic SBR), 30 (COD removal in aerobic SBR); both of these without BET	HRT: 48 h	17.1 mW/m <sup>2</sup> (anoxic), 14.3 mW/m <sup>2</sup> (aerobic) OCV: 248 and 280 mV
(Zhang et al., 2010)	MEC	Sediment	Naphtalene	100 µM (naphthalene) mixed with seawater and sediment	100 (Naphthalene)	0 (Naphtalene if heat treated) 0 (Naphtalene without electrode)	9	-
(Zhang et al., 2015)	MFC	Soil	TPHs, 16 PAHs, C8-C40 n-alkanes	25700 mg/kg dry soil	12.5 (Horizontal anodes HA),	8.3 (Vertical anodes VA) 6.4 (open circuit)	135	HA max. 0.282 V, VA max. 0.285 V, 833 coulomb accumulated for VA over the whole duration: 9 % more than in VA, current and power densities not indicated
(Zhou et al., 2016)	MFC	Soil	Petroleum hydrocarbons	20 mM	-	-	7	600 µA/cm <sup>2</sup> (6 A/m <sup>2</sup> ), 220 mW/m <sup>2</sup>

**Table 1: MFCs and MECs that are used to degrade aromatic hydrocarbons, total petroleum hydrocarbons and diesel** (If not indicated explicitly in the cited article, power and current densities ( $P/m^2$ ) are calculated by multiplication of maximum voltage and current density ( $P/m^2 = U \times I/m^2 \times 1/1000$ ) and by the quotient of maximum voltage and resistance per surface of electrode [ $I = U/R \times A$ ])

References	Species	Bacteria (Phylum, Class, Order, Family, Genus)	Hypothetical role proposed by author
(Li et al., 2014)	<i>Geobacteraceae</i> sp.	<i>Proteobacteria</i> , $\delta$ - <i>Proteobacteria</i> , <i>Desulfuromonadales</i> , <i>Geobacteraceae</i>	Electricity generation, hydrocarbon degradation
(Li et al., 2014)	<i>Escherichia</i> sp.	<i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> , <i>Enterobacteriales</i> , <i>Enterobacteriaceae</i> , <i>Escherichia</i>	Electricity generation, hydrocarbon degradation
(Li et al., 2016b)	<i>Negativicutes</i> $\delta$ - <i>Proteobacteria</i> <i>Bacilli</i>		Hydrocarbon degradation (TPH, alkane, PAH)
(Li et al., 2015)	<i>Alkanivorax</i>	<i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> , <i>Oceanospirillales</i> , <i>Alcanivoracaceae</i>	Hydrocarbon degradation
(Li et al., 2015)	<i>Proteobacteria</i> (88%, $\gamma$ - <i>Proteobacteria</i> )		Hydrocarbon degradation
(Li et al., 2015)	<i>Escherichia</i> sp.		Hydrocarbon degradation
(Lu et al., 2014a)	<i>Enterobacter cloacae</i>	<i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> <i>Enterobacteriales</i> , <i>Enterobacteriaceae</i> , <i>Enterobacter</i>	Oxidation of hexadecane and diesel
(Lu et al., 2014a)	<i>Pseudomonas</i> <i>aeruginosa</i> , <i>Pseudomonas putida</i>	<i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> , <i>Pseudomonadales</i> , <i>Pseudomonadaceae</i> , <i>Pseudomonas</i>	Electricity generation, hydrocarbon degradation
(Morris et al., 2009)	<i>Shewanella</i> sp.	<i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> , <i>Alteromonadales</i> , <i>Shewanellaceae</i> , <i>Shewanella</i>	Diesel range organics degradation
(Sabina et al., 2014)	<i>Bacillus subtilis</i> moh3	<i>Firmicutes</i> , <i>Bacilli</i> , <i>Bacillales</i> , <i>Bacillaceae</i> , <i>Bacillus</i>	Waste engine oil: long-chain, branched and cyclic hydrocarbons

(Venkidusamy et al., 2016)	<i>Shewanella</i> , <i>Rhodopseudomonas</i> , <i>Bacterioidetes</i> , <i>Clostridium</i>		Electricity generation
(Venkidusamy et al., 2016)	<i>Geobacillus</i> sp.	<i>Firmicutes</i> , <i>Bacilli</i> , <i>Bacillales</i> , <i>Bacillaceae</i> , <i>Geobacillus</i>	Diesel degradation, current generation in mediator-less MFC
(Venkidusamy et al., 2016)	<i>Megasphaera</i> sp.	<i>Firmicutes</i> , <i>Negativicutes</i> , <i>Selenomonadales</i> , <i>Veillonellaceae</i>	Diesel degradation, current generation in mediator-less MFC
(Venkidusamy et al., 2016)	<i>Flavobacterium</i> , <i>Stenotrophomonas</i> , <i>Geobacillus</i> , <i>Gordonia</i> , <i>Actinobacterium</i>	<i>Flavobacteria</i> , <i>Flavobacteriaceae</i> , <i>Flavobacterium</i> ; <i>Proteobacteria</i> , $\gamma$ - <i>Proteobacteria</i> , <i>Xanthomonadales</i> , <i>Xanthomonadaceae</i> ; <i>Firmicutes</i> , <i>Bacillis</i> , <i>Bacillales</i> , <i>Bacillaceae</i> ; <i>Actinobacteria</i> , <i>Actinomycetales</i> , <i>Gordoniaceae</i>	Diesel degradation
(Zhang et al., 2010)	<i>Geobacter metallireducens</i>	<i>Proteobacteria</i> , $\delta$ - <i>Proteobacteria</i> , <i>Desulfuromonadales</i> , <i>Geobacteraceae</i>	Toluene degradation
(Zhou et al., 2016)	<i>Ochrobactrum cicero</i> <i>Ochrobactrum intermedium</i>	<i>Proteobacteria</i> , $\alpha$ - <i>Proteobacteria</i> , <i>Rhizobiales</i> <i>Brucellaceae</i> <i>Ochrobactrum</i>	Electricity generation, petroleum hydrocarbon degradation
	<i>Geobacter sulfurreducens</i>	<i>Proteobacteria</i> , $\delta$ - <i>Proteobacteria</i> , <i>Desulfuromonadales</i> , <i>Geobacteraceae</i>	Electricity generation, petroleum hydrocarbons degradation

Table 2: MFC microbial communities involved in PAH removal

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