The use of bioelectrochemical systems in environmental remediation of xenobiotics

a review

Fernando, Eustace Y; Keshavarz, Taj; Kyazze, Godfrey

Published in:
Journal of Chemical Technology and Biotechnology

DOI (link to publication from Publisher):
10.1002/jctb.5848

Publication date:
2019

Document Version
Accepted author manuscript, peer reviewed version

Citation for published version (APA):
Fernando, E. Y., Keshavarz, T., & Kyazze, G. (2019). The use of bioelectrochemical systems in environmental remediation of xenobiotics: a review. *Journal of Chemical Technology and Biotechnology*, *94*(7), 2070-2080. https://doi.org/10.1002/jctb.5848

The use of bio-electrochemical systems in environmental remediation of xenobiotics: a review

Eustace. Y Fernando * [a, c], Taj Keshavarz [b] and Godfrey Kyazze [b]

[a] Aalborg University, Section of Biotechnology, Center for Microbial Communities, Department of Chemistry and Bioscience, Fredrik Bajers vej 7H, 9220, Denmark

[b] Faculty of Science and Technology, University of Westminster, 115 New Cavendish Street, London W1W 6UW

[c] Faculty of Applied Sciences, Rajarata University, Mihintale, Sri Lanka.

* Corresponding author

Emails : wf@bio.aau.dk, eustace6192@gmail.com

Summary

Remediation of our environment of anthropogenic pollutants has become an imperative of the 21st century in order to sustain human activity and all life on the planet. With the current limitations of the existing technologies for this purpose, the need for innovative bioremediation technologies has become vitally important. Hitherto, electrochemically active microorganisms have only been a scientific curiosity and a platform for sustainable power production from waste material. However, recent research utilizing these electrochemically active microorganisms in Bio-electrochemical systems (BES) has revealed their promising potential for bioremediation applications. The primary research focus of BES applications up-to now has been to optimize and increase their power output. The possibility of utilizing these systems for bioremediation applications has been a new facet of this field of work. This review provides a comprehensive outlook on the utilization of BES based technologies for remediation of xenobiotic environmental pollutants.

Key words: Bioelectrochemical systems, Bioremediation, Xenobiotics, Pollutants, Electroactive microorganisms

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jctb.5848

1.0. General Introduction

Anthropogenic pollution has been an environmental burden since the time humans learned to control fire and smelt metals. But, it is after the industrial revolution and the availability of synthetic chemistry, that a large variety of chemical compounds that are not normally encountered in nature, became widely available. With the gradual expansion of population centers around the world and a vast industrial supply line to provide various products and commodities to an expanding population, waste anthropogenic chemicals have already become a huge problem in the current century. Contamination of soils, sediments, ground and surface water caused by waste resulting from human action and leakage into water sources constitutes a major part of anthropogenic pollution and is a serious problem. This pollution contains compounds having toxicity and persistence which creates important concerns from health and environmental viewpoints. Moreover, it represents a significant economic burden for society. In some standard remediation strategies, for example burying polluted soils in landfills, pollutants are not destroyed and the problem is merely postponed. Chemical remediation and the disposal of contaminated waste increase the health risk for workers. Bioremediation, which uses naturally occurring microorganisms, is a more sustainable and gentle alternative to physicochemical options.

Microorganisms have developed countless strategies to depollute and detoxify their environment and to transform harmful environmental contaminants into harmless end products. However, the effectiveness of bioremediation faces a number of challenges, for instance the concentration of the contaminant, the combined biological activity of the microbial community over time and space and the consumption of energy. Unfortunately, many of the environmental pollutants released into the environment persist for long periods of time and exert their harmful effects on the biosphere for the duration of their existence. Currently available technologies are simply inadequate for rapidly removing persistent environmental pollutants from the natural environment. With the introduction and accumulation of refractory compounds in the environment, novel methods of effectively degrading and detoxifying these pollutants has become the need of the hour. Research has for example shown that within the European Union (EU), there are about 3.5 million contaminated sites with an estimated annual cost of soil decontamination in the range of EUR 10 per capita, with a range of approximately EUR 2 in Serbia to more than EUR 30 in Estonia [1]. A list of EU priority pollutants includes heavy metals, aromatic hydrocarbons e.g. polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, phenols etc. In the United States, the priority pollutants to be remediated are termed Common Contaminants of Concern (COCs) and the total estimated remediation costs in the year 1996 has been 187 billion USD. This value is likely to be much higher at present [2]. In Canada, the remediation and reclamation of polluted sites costs in the year 2015 were in the order of several hundred million Canadian Dollars [3]. For many countries in Asia, Africa and Latin America, the remediation data for costs that are incurred by environmental pollution are not readily available. Although the developing counties in aforesaid continents are likely to be the most affected by environmental damage caused by anthropogenic pollution. Left untreated contaminated sites pose a danger to human health and the environment. Hydrocarbons such as benzene are known carcinogens and contaminants can alter soil structure, inhibiting plant growth. There is need for faster, lower cost and sustainable remediation technologies to meet clean up targets and minimize risk to human health and the environment.

Bioremediation, the decontamination of polluted environments using living systems, is a sustainable, cost-effective and environmentally friendly approach to dealing with contaminated soils, sediments and groundwater [4]. However, lack of suitable and sustainable electron acceptors slows down biodegradation rate, resulting into extended treatment periods. There are other challenges too that have to be overcome. These include: (Figure 1):

a) The chemical nature of contaminant may mean that the contaminant is recalcitrant and persists in the environment;

b) Low contaminant concentrations – a threshold concentration of contaminant is often required for growth;

c) Substrate inhibition – at high concentrations some biodegradable contaminants can be toxic to the organisms that have the ability to degrade them;

d) Environmental conditions such as pH, temperature, salinity and redox potential have to be optimum for the degrading strains;

e) Indigenous strains may not have the intrinsic capability to degrade the contaminants as many need to have been pre-exposed to the contaminant they are intended to degrade in order to induce the enzymes required to accomplish the task.

Figure-1

Current industry players e.g. Regenesis, RemedX, ProxyChem, attempt to solve these problems using a number of approaches e.g. air-sparge-enhanced soil vapour extraction, steam-enhanced dual-phase extraction, biostimulation e.g. by supplying electron donors, bioaugmentation and in some instances ex-situ treatment but the costs are usually very high; for example, two oil spills in Ogoniland, Nigeria, required about $30 billion for clean-up operations over 30 years [5]. Figure 2 shows the methods commonly used to clean up contaminated soils in EU countries:

Figure-2

1.1. Electro-active microorganisms and the history of Electromicrobiology

Electromicrobiology is a recently coined term that describes a sub-discipline of microbiology that involves extracellular electron transfer (EET), from or to an insoluble electron acceptor/donor that is situated outside the microbial cell membrane. A recent comprehensive review by [6], defines the electroactive microorganism as a type of microbe that is capable of deriving all its energy by EET to an external electron acceptor, when all other potential electron acceptors are absent. Despite the recent upsurge in research pertaining to electromicrobiology, its first recorded experiments were carried out in the early 1900s by [7] and [8]. They demonstrated for the first-time that the electrons liberated by microbial oxidation of organic substrates can be channeled via external electrical circuits to suitable electron acceptors located outside of microbial cells. Following the pioneering work by the aforesaid researchers in this field, the enthusiasm and therefore, the amount of related research dried up, until the early 1980s. The 1970s and the years that followed renewed the debate on alternative forms of energy, due to the crises in the fossil fuel industry at that time. This renewed enthusiasm in alternative energy forms that included bioenergy, propelled a new wave of research in electromicrobiology. With that, came a new understanding about electro-active microorganisms and their EET mechanisms from studies such as [9] and [10]. Since then, the number of publications has grown exponentially on this area of research. The primary focus of electromicrobiology related research has always been on microbial fuel cells (MFCs), where bio-electrochemical reactions driven by microbes can be exploited to harness energy from organic substrates. A sizable proportion of related work also discuss the importance of electromicrobiology in biogeochemical cycles [11, 12]. Deciphering the mechanisms of microbial EET also attracted much attention and contributed to many publications in this field [13, 14].

Another more recently identified and an interesting facet of electromicrobiology is that its use in environmental remediation. This aspect however, is vastly overshadowed by the amount of work conducted in MFCs, their power optimization studies, electron transfer mechanism studies and their potential applications. Hence, it is fair to state that the work conducted on application of electromicrobiology in environmental remediation is somewhat limited. Hitherto, there has been no comprehensive review on this aspect of electromicrobiology. Therefore, the purpose of this review is to provide a comprehensive understanding on the state of the art of the applications of electromicrobiology in environmental remediation.

1.2. Microbial electron transfer in environmental remediation

Anthropogenic environmental pollution is the introduction of contaminants (including xenobiotic compounds) into the natural environment as a result of human activity [15]. Microbial environmental remediation in the conventional sense implies that the use of microorganisms in degradation, detoxification and ultimately, removal of xenobiotic compounds from the environment [16]. Similarly, environmental remediation by electro-active microorganisms can be described as microbes utilizing EET to conduct (or EET that may result in) degradation and detoxification of environmental pollutants. Remediation of xenobiotics with the use of electroactive microorganisms in BES is a very recent development and there have been no published examples of this prior to the 2000s. Myriad different environmental pollutants contained in soil, surface water or ground water can be treated by microorganisms. Environmental decontamination of pollutants by microorganisms follow many biochemical pathways and the mechanisms of degradation and detoxification of various classes of environmental pollutants are extensively discussed in other reviews [16, 17, 18]. Similarly, EET mechanisms aid microbes to perform degradation of various pollutants as well as corrosion of metal containing waste material. The debate on extracellular electron transfer from microbial metabolism onto various electron acceptors (such as metal oxides and electrodes) situated outside electroactive microorganisms has not been settled yet. Several different mechanisms are currently proposed for EET. These include direct electron transfer either by direct cellular contact to the external electron acceptor or electron transfer via conductive pilli-like appendages known as nanowires. The other major EET mechanism proposed is electron shuttling via redox mediators such as flavin and humic acid compounds. It is generally accepted that electroactive microorganisms such as *Geobacter* spp. predominantly utilize direct electron transfer mechanisms such as nanowires, whereas certain other electroactive microorganisms such as *Pseudomonas* spp. and *Shewanella* spp. prefer to use electron shuttling mechanisms for EET [19, 20].

When xenobiotic pollutants are acting as extracellular terminal acceptors, it is likely that they also undergo reduction via the same electron shuttling mechanisms. Azo class dye pollutants can be shown as an example. Due to their large size and highly charged nature, they are unlikely to cross biological membranes into cellular interior. Therefore, EET from electroactive microorganisms is likely to proceed via electron shuttling redox compounds [21]. Electron transfer onto the azo moiety of azoic pollutants results in their effective degradation and color removal. However, detailed research into this area to understand the EET mechanisms of xenobiotic removal is still at its infancy. Therefore, it is vital that more research efforts are devoted to this area to understand and to better control xenobiotic removal using electroactive microorganisms.

1.3. Types of environmental pollutants remediated by microbial EET

Readily biodegradable compounds such as volatile fatty acids (e.g. acetate, butyrate and propionate), sugars (e.g. glucose), proteins and amino acids among others are easily converted to simpler compounds (or mineralized) by electroactive microorganisms in their natural habitat or in bioelectrochemical systems (BES). Aforesaid compounds are rapidly transported within the electroactive microbial cells and are then catabolized as substrates to produce metabolic energy and electrons, that are subsequently transferred outside the cell, to various electron acceptors. This results in their eventual degradation and removal from the environment. The catabolic degradation and liberation of metabolic electrons by some of the representative organic compounds is shown below:

$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$ (Sucrose) ------- (1)

$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9\,H^+ + 8\,e^-$ (Acetate) --------(2)

The conversion and the bioenergetics of readily biodegradable contaminants (i.e. substrates) by various electroactive microorganisms is well described and are extensively covered in other research and review articles [22, 23]. This review will only focus on conversion and remediation of more recalcitrant contaminants of xenobiotic nature, by electroactive microorganisms.

Xenobiotic pollutants on the other hand, gets converted at much slower rates and their conversion mechanisms differ from the readily degradable environmental pollutants. The mechanism of biochemical transformations of environmental contaminants depends mainly on the chemical properties of the pollutants themselves and the EET potential of the electroactive microorganisms. Xenobiotics are not compounds that are naturally encountered by microorganisms. Therefore, it is unlikely that they are readily taken-up into the cellular interior by microorganisms and may partly contribute to their recalcitrance. Therefore, it is preferable that the xenobiotic compounds are treated outside the cells and the utilization of EET mechanisms would be greatly beneficial in this regard. Studies conducted in the past two decades have shed light on the remediation of many different types of xenobiotic environmental pollutants by microbial EET, which will be discussed in detail in this section.

1.4. Types of BES used for remediation of environmental pollutants

Although the application of BES in environmental remediation of xenobiotics is relatively new, a variety of BES types were hitherto employed in this area of work. Examples of such systems include different designs of MFCs (two-chamber, mono-chamber, up-flow continuous set-up) [24, 25, 26], Microbial Electrolysis Systems (MES) [27], benthic/sediment based microbial fuel cells [28], constructed wetland based MFCs [29], U-tube type soil MFCs [30] and many combinations of BES and other systems such as BES – up-flow anaerobic sludge blanket (BES-UASB) set-ups [31]. The choice and application of certain set-ups seems to confer various benefits over other systems. For example, unique BES types such as benthic/sediment MFCs and constructed wetland-BES systems appear to be the best suited systems to remediate xenobiotic compounds in-situ, outside laboratory environments. While the conventional two-chamber MFC and MEC systems seem to be best for laboratory-based proof of concept studies of xenobiotic removal, they offer only limited advantages when it comes to in-situ application. Li et al., 2017 [32] provides an extensive review on the types of MFCs that are hitherto utilized to remediate various environmental pollutants, especially pertaining to pollutant remediation in soils (Figure-3). Examples of such BES range from U-tube type, column type and multi-anode type, capable of treating pollutants such as petroleum hydrocarbons, dibenzothiophene, phenol and hexachlorobenzene.

Figure - 3

Electrodes inserted in soil could increase oxidant delivery to support anaerobic biodegradation of organic compounds in soils and sediments [33] in microbial fuel cells. MFCs are unique in the sense that the microorganisms are able to transfer (or receive) electrons extracellularly to a solid material like an anode electrode. The use of oxygen as an indirect terminal electron acceptor would be expected to enhance hydrocarbon degradation compared to degradation via anaerobic respiration. MFCs are a new technology for remediation of soils contaminated with organic compounds without need for in situ addition of any electron donor or electron acceptor into the soil or subsurface environment. Moreover, electricity production during MFC operation can serve as a real-time bioremediation indicator and also power wireless sensors for remote online monitoring. The electrodes have no negative environmental effects during their production and can be made from cheap materials such as biochar.

2. Advantages of using BES in bioremediation

Numerous studies have demonstrated that bioremediation of different types of environmental pollutants proceeds at accelerated rates in BES, compared to their non-BES counterparts. Many of these studies that were discussed later in this review, have shown to remediate various classes of xenobiotic environmental pollutants at several folds higher rates than their non-BES counterparts. The main driver behind this accelerated kinetics of pollutant biotransformation is thought to be the elevated rates of metabolism of electrochemically active microorganisms in BES environments [34, 35]. The main reason for this is that in BES environments, the microbial metabolism is not limited by the supply of the terminal electron acceptor. Therefore, the absence of terminal electron acceptors is unlikely to be a rate-limiting factor for microbial metabolism in efficient BES. This in turn, would lead to efficient pollution conversion kinetics in BES. Domininguez-Garay et al., 2018 [36], concluded that using electrodes at a positive potential [+600 mV (versus Ag/AgCl)] atrazine mineralization was enhanced by 20‐fold when compared to natural attenuation in electrode‐free controls. Furthermore, ecotoxicological analysis of the soil after the bioelectrochemical remediation treatment revealed an effective clean‐up in < 20 days. In natural environments such as sediments, soil and laboratory non-BES reactors, various terminal electron acceptors such as NO_3^-, SO_4^{2-}, molecular oxygen and other organics are utilized to sustain microbial metabolism. However, the actual availability of such electron acceptors can be greatly diminished due to low concentrations and diffusion limitations (especially molecular oxygen due to its low water solubility). Electrochemically active microorganisms in BES on the other hand, rely on an artificially poised electrode to divert their metabolic electrons. In other words, an electrode serves as the terminal electron acceptor, thus circumventing the limitation of terminal electron acceptor unavailability.

When comparing the application of BES to conventional electrochemical destruction of pollutants, it is clear that microbially-assisted electrochemical conversion of many xenobiotic pollutants requires substantially less amounts of electrical energy. Electrochemically active microorganisms themselves in BES act as catalysts for electron transfer onto various electrode surfaces in the BES, as well as pollutant molecules that are targeted for bioconversion.

In addition to this, BES such as MFC systems offer the attractive prospect of sustainable energy production in the form of biogenic electricity. With the advancing understanding of the BES systems, better, innovative and more efficient BES designs are being made available and this offers great advantages for environmental pollutant remediation. Moreover, the unit cost of many BES systems are becoming cheaper, with the advent of new and cheap electrode types, ion permeable membranes and cheaper electrode catalysts such as phthalocyanin and granular activated carbon catalysts [37, 38]. This reduction of procurement, deployment and maintenance costs will greatly increase the environmental applicability of such BES systems in real-world contaminated sites.

3. Types of xenobiotic organic pollutants remediated by BES

Azo dyes

Azo dyes by far, is the most widely studied class of environmental pollutant that is remediated by electroactive microorganisms. Azo dyes are characterized by one or more of the azo moieties, which are of oxidative nature. Therefore, the most obvious conversion mechanism of azo dyes by electroactive microorganisms is by the azo pollutant acting as an electron acceptor and undergoing reduction into their constituent amines. Azo moieties are flanked by R groups which may contain various electron rich or electron poor substituent groups, which would influence the redox potential of the dye.

Sun et al., 2009 [39], for the first time demonstrated that a mixture of aerobic anaerobic sludge, when used in a single-chamber microbial fuel cell (MFC) can rapidly convert the model azo dye Brilliant Red X-3B. Since then, many studies have demonstrated using a many different azo dyes that they can be degraded to their constituent amines by electroactive microorganisms. Primarily among these, in a pure culture study, [24] for the first time demonstrated that the electroactive microorganism *Shewanella oneidensis* could rapidly degrade the commercial azo dye Acid Orange-7 (AO7) when included as a co-substrate in an MFC anode. Similarly, subsequent study by the same group demonstrated that complex, commercially-used azo dye mixtures can be rapidly degraded by a complex thermophilic anodic microbial community in two-chamber MFCs [40].

The mechanism of azo dye degradation in MFC anodes is generally accepted to be via the reduction of the azo chromophore [24] (figure-4).

Figure - 4

Azo bonds themselves are electron-withdrawing in nature and the chemical substituent groups flanking the azo moiety highly influences the overall redox potential of the azo dye [21]. If the flanking chemical substituents are also electron-withdrawing in in nature, they would render the azo dye highly electron withdrawing (high – redox potential) and therefore, will readily undergo reductive degradation [41]. The higher the redox potential of an azo compound, the better it would act as an electron acceptor for electroactive microorganisms. Many commercial azo dyes are of large molecular weights (300 Da – 1.5 kDa) and contain highly charged substituent groups [41, 42]. Therefore, they are unlikely to penetrate biological membranes into cellular interior [40]. Therefore, azo dyes with a high-enough redox potential, generally are good candidates for EET by electroactive microorganisms growing in a planktonic culture. The fact that azo dye reductive degradation follows faster kinetic rates in presence of electroactive microorganisms, compared to other degradation mechanisms (i.e. enzymatic or mediator driven) was first demonstrated by [24]. Results of that study indicated that the reductive degradation kinetics of the azo dye AO7 is markedly faster under the electroactive microorganism *S.oneidensis*, in an MFC set-up, compared to the degradation kinetics of the same dye with anaerobically digested sludge. It was also shown in the same study that AO7 degradation kinetics can be enhanced by supplementing anaerobically digested sludge with a *S.oneidensis* pure culture, in an anodic compartment of MFC experimental set-up (figure-5).

Figure - 5

Further manipulation of AO7 reductive degradation kinetics of several azo dyes was demonstrated by the same group by applying various external resistances (R_{ext}) to dye-containing MFC set-ups [43]. It was demonstrated in the aforesaid study that, by using an R_{ext} that closely resembles the internal resistance (R_{int}) of the MFC system, higher EET rates can be achieved – leading to rapid reductive degradation of azo dyes in the anodic compartment. This is further evidence that supports the notion that EET capable microorganisms can positively influence reductive azo dye conversion.

Others have demonstrated that different modifications and add-on systems to BES such as MFC coupled constructed wetland systems [44], MFC biocathodes [45] and microbial electrolysis systems [46] can be used to efficiently convert azo dyes.

Nitrobenzene compounds

Under reductive conditions, Nitrophenol compounds undergo transformation by addition of electrons and protons, into the corresponding amine [29]. It was demonstrated that abiotic cathodic removal of 2-nitrophenol [29] and removal of parafluoronitrobenzene by a biocathode (Shen et al., 2014) was possible. Feng et al., 2011 [29] utilized the Fe (II)/Fe (III) redox couple (added in the form of Fe (II)) can significantly enhance the reductive removal kinetics of 2-nitrophenol in the abiotic cathode. Although this can be considered as partial biotransformation of the aforesaid compounds into their constituent amines, the resultant transformation products are more amenable to further biodegradation than their parent compounds under suitable conditions [47].

Chloronitrobenzene compounds

Various industries ranging from dyes, explosives and pharmaceuticals utilize Chloronitrobenzene compounds (CNBs) CNB compounds are known to be toxic and highly recalcitrant [31]. However, a recent study utilizing BES coupled up-flow anaerobic sludge blanket (UASB) system demonstrated that CNBs can effectively be transformed to relatively more biodegradable end products.

Figure - 6

A CNB compound, 2,4-dintrochlorobenzene underwent de-halogenation and reductive transformation of nitro groups into amine groups. CNBs are known to be highly electron-withdrawing in nature. Therefore, it can be expected that 2,4-nitrochlorobenzene may accept electrons from electrochemically active microorganisms and undergo reductive transformation in BES based bioreactor systems.

Chlorinated aromatics are particularly known to be resistant to biotransformation. Therefore, a more significant outcome of this work was that de-chlorination of 2,4-dintrochlorobenzene also took place (figure-6).

Microbial community analysis of the samples of UASB-BES system of the aforesaid study revealed that the dominant microorganisms that are present were *Acetobacterium* spp (11.62%), *Arcobacter* spp. (13.53%) and *Desulfovibrio* spp. (4.42%). Others enriched in the UASB-BES reactor, in comparison to the UASB control reactor were *Comomonas* spp (2.07%), *Denitrovibrio* spp (1.96%), *Petrimonas* spp (1.06%). Organisms belonging to genera such as *Arcobacter* spp, *Desulfovibrio* spp and *Comomonas* spp were earlier demonstrated to be capable of EET [48, 49, 50].

Polychlorobiphenyl compounds (PCBs) and halocarbon compounds

Several previous studies [33, 51, 52, 53] demonstrated that PCBs and halocarbon compounds can effectively be bioremediated by electrochemically active microorganisms in BES. In the two studies Aulenta et al., 2007 [31] and Aulenta et al., 2011 [51], it was demonstrated that bioelectrochemical systems that are operating with a controlled cathode potential, ranging from -250 mV to -750 mV could rapidly conduct microbially-induced reductive de-chlorination of trichloroethene (TCE) – a halocarbon compound. It was demonstrated in the same two studies that when the cathode was poised to around -250 mV, methanogenesis was almost completely suppressed and the electron diversion efficiency towards the TCE dichlorination reaction was close to 95%. A similar study also demonstrated that a similar halocarbon – cis-dichloroethene can also be reductively bioremediated using a BES set-up [52]. Similarly, 1,2 – dichloroethane was shown to be utilized as the electron donor of an anodic mixed microbial community, by Pham et al., 2009 [54]. PCBs are known to be highly toxic and carcinogenic environmental pollutants [55]. In a recent study conducted by [53] demonstrated that PCB degradation in benthic BES systems. The most important aspect of the work conducted by Chun et al., 2013 [53] was that in-situ PCB degradation was achieved with an applied voltage (1.5V – 3V), under non-laboratory conditions. Both naturally weathered PCBs and artificially spiked PCBs were used for the study and both oxidative and reductive biotransformations were achieved in the benthic BES system. Application of higher voltages favored initial de-chlorination, followed by formation and eventual consumption of chlorobenzoate – suggesting oxidative degradation of PCBs. Other halogenated compounds such as hexachlorobenzene [56] and Lindane [57] were also effectively degraded and detoxified in several previous studies, employing soil-based BES. Chlorinated organics such as hexachlorobenzene and lindane are known to be very recalcitrant and to have long half-lives (2.6 – 22.9 years in soil) in the environment [56]. In the study conducted by Cao et al., 2015 [56], hexachlorobenzene degradation rates of up-to 71% were achieved in 56 days of BES operation (hexachlorobenzene concentrations ranging from 40 mg/kg – 200 mg/kg in soil). Considering the refractory nature such halogenated organics, the accelerated degradation of them in BES (compared to conventional systems) is highly significant. These studies clearly demonstrate the very promising potential of BES systems to effectively and rapidly bio-transform these recalcitrant environmental pollutants. They also demonstrated that pollutant transformation can be achieved in a relatively eco-friendly manner by using BES based systems, compared to conventionally used physico-chemical environmental remediation methods.

Petroleum compounds and Polyaromatic hydrocarbons (PAHs)

Petrochemical compounds, aryl and aromatic hydrocarbons (including PAHs) were also the subject of investigation in various types of BES based systems, in several recent studies. Petrochemical compounds, especially PAHs are known to be resistant to biodegradation. It is an attractive avenue to utilize hydrocarbon pollutants as the electron donor in MFC systems, where concomitant power production and oxidation of the hydrocarbon pollutant can be achieved. It was first demonstrated by [58 and 59], where diesel (mixtures of aliphatic hydrocarbons ranging in from C-8 to C-25) anaerobic biodegradation was shown to be significantly enhanced by MFCs, compared to their anaerobic reactor controls (82% in MFC compared to 31% hydrocarbon degradation in the anaerobic control). A study conducted by [60] attempted to mimic polluted soil by conducting MFC experiments in PAH and aryl hydrocarbon contaminated saline soil. A U-tube type MFC was used for this study where, a simultaneous power production and hydrocarbon removal was achieved. Since then, many different types of BES, employing several types of inocula and hydrocarbon pollutants demonstrated the possibility of successful biodegradation of hydrocarbons, including the recalcitrant PAHs. Furthermore, it was demonstrated by Lin et al., 2014 [61] that benzene, toluene, ethylbenzene and xylene (BTEX) mixtures degrades via anoxic oxidation pathways in MFC experiments. When toluene was used as the sole source of carbon and energy in MFC experiments, toluene degradation proceeded via benzoic acid as the transformation product, and later leading to complete consumption of benzoic acid. This BTEX mixture, supplied as the sole electron donor to the MFC system produced a concomitant power output at around 3 mWm^{-2}. The importance of inoculum type in MFC based degradation of phenanthrene was demonstrated by [62], where pure culture studies utilizing *Shewanella oneidensis* MR1 14063, *Pseudomonas aeruginosa* NCTC 10662 and combinations of both (defined co-cultures) were conducted. All the investigated pure and co-cultures resulted in very high phenanthrene rates- over 97%, with concomitant power outputs averaging 1.25 mWm^{-2}. In a study conducted by [63], an in-situ experiment was conducted on PAH containing river sediments using an innovative “snorkel” type cathode. It was demonstrated that different redox zones can be bridged by using this snorkel type electrode, where atmospheric oxygen could be channeled to the electrode dwelling microbial community, without disrupting the anoxic redox conditions that prevail in the bulk river sediment. The key-findings of this study suggests that biogeochemical reactions that takes place in the river sediment can be expedited by the channeling of a constant supply of terminal electron acceptor (O_2) via a snorkel electrode into the system. As a result of expedited microbial activity and biogeochemical reactions taking place in the anaerobic sediment, PAHs, among other electron donors become remediated at an elevated rate.

Table - 1

Remediation of other organic pollutants by BES

Other types of environmental pollutants such as pesticides have also been demonstrated to be degraded and detoxified with the aid of BES systems. In an innovative study recently conducted by [36], it was shown that the pesticide Atrazine was mineralized 20-fold faster, when BES systems were employed, compared to their non-BES controls. The soil-based BES system was supplemented with ^{14}C labelled Atrazine as the sole electron donor for the microbes and the working electrode was poised at 600 mV (vs Ag/AgCl reference), acted as a terminal electron acceptor for the microbial mineralisation of ^{14}C labelled Atrazine. In a separate study [64], demonstrated the use of insertion type soil MFCs to achieve phenol degradation coupled to simultaneous power output of around 30 mW/m2. In the same study, it was demonstrated that the phenol degradation in the soil MFC system proceeds approximately 23 times faster compared to its standalone anaerobic control. Other less toxic organic pollutants such as furfural (an inhibitor of ethanol formation from lignocellulosic materials) were demonstrated to be utilized as the sole electron donor in MFC anodes for a maximum power output of 103 Wm/m^3, by [65]. In addition to this, [66] demonstrated the use of BES for effective removal of endocrine disruptive micropollutants such as estrogen compounds.

4. Remediation of inorganic environmental pollutants using BES

Chlorate and Bromate derivatives

Chlorate, perchlorate and bromate derivatives are increasingly becoming an environmental problem because they are present in significant concentrations in groundwater reserves in certain parts of the world [67, 68]. Chlorate and bromate derivatives are known human carcinogens and are highly toxic [69]. Therefore, the technologies that are capable of effectively converting these pollutants are of much value. In an interesting previous study, [70] utilized an innovative concentric-type tubular up-flow MFC system to simultaneously remediate two pollutants. In the anode, aromatic hydrocarbon compounds such as phenanthrene and benzene were used as the sole source of carbon and electron donor for electroactive microorganisms. The inner concentric catholyte of the system contained bromate as the electron acceptor. Bromate has a very high redox potential (1.4 V vs SHE) and is capable of readily accepting electrons and undergoing reduction into bromide (Br^{-1}) ions [70]. The system was capable of hydrocarbon removal in the anode in excess of 90%, whereas, the simultaneous bromate reduction in the catholyte was in excess of 79%. The removal of both these types of pollutants in the same system, while producing a power output around 7 mWm^{-2}, is a significant outcome of this study. Perchlorate ions were bioelectrochemically reduced using a denitrifying biocathode BES in a study conducted by [68]. A perchlorate reduction rate of 24 mg/L/day at a conversion efficiency of 84% was achieved without the aid of exogenous redox shuttling compounds. In a similar study conducted by [71] demonstrated that high-concentrations (90 mg/L) of perchlorate can be effectively reduced in microbially assisted electrochemical reactors utilizing a co-culture of *Dechloromonas* spp and *Azospira* spp, with the addition of the redox shuttle 2,6-anthraquinone disulfonate (AQDS). In addition to the toxic inorganic chemical removal, nutrient removal and recovery such as nitrogen and phosphorus using BES systems was discussed in [72].

Detoxification and immobilization of heavy metals

A limited number of previous BES studies were directed towards investigating inorganic environmental pollutants such as heavy metals. Heavy metals are important environmental pollutants that has the potential to accumulate up the food chains and cause great damage to the flora and fauna exposed to them. Therefore, it is imperative to seek innovative methods to immobilize and detoxify free heavy metals that are released to the environment as a result of anthropogenic activity. The main current methods used for capturing heavy metals from pollutant environments include the use of sorbents (including biosorbents) [73] and electrochemical reduction [73]. Electrochemical reduction requires the input of substantial amounts of electrical energy into the polluted environment and therefore, is expensive. The use of sorbents raises the need to regenerate the sorbent for repeated use. This could be difficult and may require the need for the input of various other chemicals (to release the bound heavy metals from the sorbent) that may present treatment and disposal problems of their own. Previously, [74] demonstrated that Cr^{6+} present in electroplating wastewater can be successfully reduced and recovered in an MFC cathode, with a simultaneous power production of 1600 mW/m^{-2}. Similarly, a study conducted by [75] demonstrated that copper ions can be reduced and recovered in its metallic form at a two-chambered MFC system. These findings are indicative of the promising potential of BES to immobilize and to recover heavy metal ions from contaminated environments.

5. Perspectives and outlook

From the current research pertaining to bioremediation of environmental pollutants using BES, it becomes evident that these systems are very promising candidates for in-situ and ex-situ environmental remediation applications. It is also apparent from the current research that tailor-made and customized BES can be employed to remediate a wide range of environmental pollutants belonging to many different classes of chemicals. Some of the most refractory chemicals that are otherwise known to persist under other types of biotic treatment, have shown to undergo rapid degradation in BES by electrochemically active microorganisms. The most attractive aspects of bioremediation using BES systems are that BES systems are more environmentally acceptable compared to most physico-chemical remediation methods and that high pollutant biotransformation rates can be achieved using BES. There is also a prospect of biogenic electricity production if MFC based systems are used for bioremediation.

New and more innovative BES designs such as constructed wetland based, U-tube, concentric type, multi-anode systems are becoming available, making their scalability and operating/installation costs much more relevant for in-situ/ex-situ application at contaminated sites. The other benefit of BES based methods is that they can be readily combined with other systems such as BES-UASB [31], BES-activated sludge systems [26, 40] to broaden the range of pollutants dealt with or to achieve a more complete biotransformation of pollutants into non-toxic end products. Therefore, combinations of BES and other bioremediation methods has become an attractive prospect for further research to remediate a large range of environmental pollutants efficiently.

Electrochemically active microorganisms (including fungi) and their biochemical mechanisms that drive such biotransformation of xenobiotics however, remain poorly understood. Only a few mechanistic studies were hitherto conducted to shed more light on underlying biochemical basis of pollutant biotransformation in BES. Therefore, a more focused research effort will be useful in understanding such mechanisms and ultimately making BES more efficient in environmental pollutant remediation.

BES based pollutant remediation often involves complex microbial communities containing a number of different electrochemically active microorganisms carrying out the vital electron transfer mechanisms and another set of equally important microorganisms conducting all the other supporting biochemical reactions. The end-result of pollutant removal is often the result of summation of all the activities of the whole microbial community. However, the microbial community structure in many of the BES based pollutant remediation studies conducted previously, remains largely unknown. This is partly because not much research efforts have been focused on microbial community profiling of BES bioremediation experiments using modern sequencing techniques such as NGS (next-generation sequencing platforms such as Illumina, NanoPore and Ion-Torrent) methods. This could be due to high costs of these sequencing technologies. Therefore, it is imperative to focus more research efforts into understanding the community structures of BES based bioremediation experiments. The information about identities and relative abundances of key microbial players in such experiments would pave the way for assigning functionalities to some of the key microbes. This information would eventually lead to better optimization of BES based bioremediation efforts.

Hitherto, there have been a few examples of commercial application of this very new technology for large-scale remediation of xenobiotics. One of the forerunners has been a company known as Emefcy, where modular large-scale MFC units were utilized as standalone or supplementary wastewater treatment systems for pollutant removal (Emefcy has now merged with RWL water to form Fluence Global water and Wastewater Solutions). Other examples include companies such as Cambrian Innovation (with the proprietary EcoVolt wastewater treatment system), Prongineer and Triqua International BV are several of the current commercial providers of large-scale MFC based remediation technologies. Several current challenges remain for the application of BES based technologies to remediate contaminated sites. These include high cost of essential material for BES construction (such as electrode material, catalysts and ion selective membranes) and scalability issues. However, despite the aforesaid challenges, BES remain one of the most promising platforms to tackle the problem of remediating xenobiotic environmental pollutants in an eco-friendly and a sustainable manner.

6. Acknowledgements

EF was funded by NomiGas and RecoverP projects at Aalborg University

7. References

[1] European Environment Agency., 2018 [online] Available at; https://www.eea.europa.eu/highlights/soil-contamination-widespread-in-europe . Accessed on 21-06-2018

[2] US Environment Agency., 2017 [online] Available at; https://www.epa.gov/enforcement/enforcement-annual-results-numbers-glance-fiscal-year-2017 . Accessed 18-09-2018

[3] Canadian Environment Assessment Agency., 2017 [online] Available at; https://www.canada.ca/en/environment-climate-change/services/federal-contaminated-sites/funding.html . Accessed 19-09-2018.

[4] US Environment Agency., 2018 [online] Available at; https://www.epa.gov/remedytech/remediation-technology-descriptions-cleaning-contaminated-sites . Accessed 19-09-2018

[5] US Environment Agency., 2018 [online] Available at; https://www.unenvironment.org/explore-topics/disasters-conflicts/where-we-work/nigeria/environmental-assessment-ogoniland-report . Accessed 19-09-2018.

[6] Koch C, Harnisch F. Is there a specific ecological niche for electroactive microorganisms? ChemElectroChem. 2016;3(9):1282-95.

[7] Potter MC. Electrical effects accompanying the decomposition of organic compounds. Proc R Soc Lond B. 1911;84(571):260-76.

[8] Cohen B. The bacterial culture as an electrical half-cell. J Bacteriol. 1931;21(1):18-9.

[9] Lovley DR, Phillips EJ. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Applied and environmental microbiology. 1988;54(6):1472-80.

[10] Myers CR, Nealson KH. Microbial reduction of manganese oxides: interactions with iron and sulfur. Geochimica et Cosmochimica Acta. 1988;52(11):2727-32.

[11] Lovley DR. Electromicrobiology. Annual review of microbiology. 2012;66:391-409.

[12] Sun D, Wang A, Cheng S, Yates M, Logan BE. Geobacter anodireducens sp. nov., an exoelectrogenic microbe in bioelectrochemical systems. International journal of systematic and evolutionary microbiology. 2014;64(10):3485-91.

[13] Logan BE. Exoelectrogenic bacteria that power microbial fuel cells. Nature Reviews Microbiology. 2009;7(5):375.

[14] Schröder U. Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency. Physical Chemistry Chemical Physics. 2007;9(21):2619-29.

[15] Torres MA, Barros MP, Campos SC, Pinto E, Rajamani S, Sayre RT, et al. Biochemical biomarkers in algae and marine pollution: a review. Ecotoxicology and Environmental Safety. 2008;71(1):1-15

[16] Das M, Adholeya A. Role of Microorganisms in Remediation of Contaminated Soil. In: Satyanarayana T, Johri BN, editors. Microorganisms in Environmental Management: Microbes and Environment. Dordrecht: Springer Netherlands; 2012. p. 81-111.

[17] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource technology. 2001;77(3):247-55.

[18] Wilson SC, Jones KC. Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs): a review. Environmental pollution. 1993;81(3):229-49.

[19] Schröder U. Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency. Physical Chemistry Chemical Physics. 2007;9(21):2619-29.

[20] Rabaey K, Verstraete W. Microbial fuel cells: novel biotechnology for energy generation. TRENDS in Biotechnology. 2005;23(6):291-8.

[21] Pandey A, Singh P, Iyengar L. Bacterial decolorization and degradation of azo dyes. International Biodeterioration & Biodegradation. 2007;59(2):73-84.

[22] Pant D, Van Bogaert G, Diels L, Vanbroekhoven K. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresource technology. 2010;101(6):1533-43.

[23] Rahimnejad M, Adhami A, Darvari S, Zirepour A, Oh S-E. Microbial fuel cell as new technology for bioelectricity generation: a review. Alexandria Engineering Journal. 2015;54(3):745-56.

[24] Fernando E, Keshavarz T, Kyazze G. Enhanced bio-decolourisation of acid orange 7 by Shewanella oneidensis through co-metabolism in a microbial fuel cell. International Biodeterioration & Biodegradation. 2012;72:1-9

[25] Liu H, Ramnarayanan R, Logan BE. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environmental science & technology. 2004;38(7):2281-5.

[26] Fernando E, Keshavarz T, Kyazze G, Fonseka K. Treatment of colour industry wastewaters with concomitant bioelectricity production in a sequential stacked mono-chamber microbial fuel cells–aerobic system. Environmental technology. 2016;37(2):255-64.

[27] Jeremiasse AW, Hamelers HV, Buisman CJ. Microbial electrolysis cell with a microbial biocathode. Bioelectrochemistry. 2010;78(1):39-43.

[28] Gong Y, Radachowsky SE, Wolf M, Nielsen ME, Girguis PR, Reimers CE. Benthic microbial fuel cell as direct power source for an acoustic modem and seawater oxygen/temperature sensor system. Environmental science & technology. 2011;45(11):5047-53.

[29] Feng C, Li F, Sun K, Liu Y, Liu L, Yue X, et al. Understanding the role of Fe(III)/Fe(II) couple in mediating reductive transformation of 2-nitrophenol in microbial fuel cells. Bioresource Technology. 2011;102(2):1131-6

[30] Wang X, Cai Z, Zhou Q, Zhang Z, Chen C. Bioelectrochemical stimulation of petroleum hydrocarbon degradation in saline soil using U‐tube microbial fuel cells. Biotechnology and Bioengineering. 2012;109(2):426-33.

[31] Jiang X, Shen J, Han Y, Lou S, Han W, Sun X, et al. Efficient nitro reduction and dechlorination of 2, 4-dinitrochlorobenzene through the integration of bioelectrochemical system into upflow anaerobic sludge blanket: a comprehensive study. Water research. 2016;88:257-65.

[32] Li W-W, Yu H-Q. Stimulating sediment bioremediation with benthic microbial fuel cells. Biotechnology Advances. 2015;33(1):1-12.

[33] Aulenta F, Catervi A, Majone M, Panero S, Reale P, Rossetti S. Electron transfer from a solid-state electrode assisted by methyl viologen sustains efficient microbial reductive dechlorination of TCE. Environmental science & technology. 2007;41(7):2554-9.

[34] He Z, Minteer SD, Angenent LT. Electricity generation from artificial wastewater using an upflow microbial fuel cell. Environmental science & technology. 2005;39(14):5262-7.

[35] Rabaey K, Verstraete W. Microbial fuel cells: novel biotechnology for energy generation. TRENDS in Biotechnology. 2005;23(6):291-8.

[36] Domínguez-Garay A, Boltes K, Esteve-Núñez A. Cleaning-up atrazine-polluted soil by using Microbial Electroremediating Cells. Chemosphere. 2016;161:365-71.

[37] Zhao F, Harnisch F, Schröder U, Scholz F, Bogdanoff P, Herrmann I. Application of pyrolysed iron (II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. Electrochemistry Communications. 2005;7(12):1405-10.

[38] Deng Q, Li X, Zuo J, Ling A, Logan BE. Power generation using an activated carbon fiber felt cathode in an upflow microbial fuel cell. Journal of Power Sources. 2010;195(4):1130-5.

[39] Sun J, Hu Y-y, Bi Z, Cao Y-q. Simultaneous decolorization of azo dye and bioelectricity generation using a microfiltration membrane air-cathode single-chamber microbial fuel cell. Bioresource Technology. 2009;100(13):3185-92.

[40] Fernando E, Keshavarz T, Kyazze G. Simultaneous co-metabolic decolourisation of azo dye mixtures and bio-electricity generation under thermophillic (50°C) and saline conditions by an adapted anaerobic mixed culture in microbial fuel cells. Bioresource Technology. 2013;127:1-8.

[41] Gottlieb A, Shaw C, Smith A, Wheatley A, Forsythe S. The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. Journal of Biotechnology. 2003;101(1):49-56.

[42] Hsueh C-C, Chen B-Y, Yen C-Y. Understanding effects of chemical structure on azo dye decolorization characteristics by Aeromonas hydrophila. Journal of hazardous materials. 2009;167(1-3):995-1001.

[43] Fernando E, Keshavarz T, Kyazze G. External resistance as a potential tool for influencing azo dye reductive decolourisation kinetics in microbial fuel cells. International Biodeterioration & Biodegradation. 2014;89:7-14

[44] Fang Z, Song H-l, Cang N, Li X-n. Electricity production from Azo dye wastewater using a microbial fuel cell coupled constructed wetland operating under different operating conditions. Biosensors and Bioelectronics. 2015;68:135-41

[45] Sun J, Bi Z, Hou B, Cao Y-q, Hu Y-y. Further treatment of decolorization liquid of azo dye coupled with increased power production using microbial fuel cell equipped with an aerobic biocathode. Water research. 2011;45(1):283-91.

[46] Mu Y, Rabaey K, Rozendal RA, Yuan Z, Keller J. Decolorization of azo dyes in bioelectrochemical systems. Environmental science & technology. 2009;43(13):5137-43.

[47] Jiang X, Shen J, Han Y, Lou S, Han W, Sun X, et al. Efficient nitro reduction and dechlorination of 2, 4-dinitrochlorobenzene through the integration of bioelectrochemical system into upflow anaerobic sludge blanket: a comprehensive study. Water research. 2016;88:257-65.

[48] Lu L, Xing D, Ren N. Pyrosequencing reveals highly diverse microbial communities in microbial electrolysis cells involved in enhanced H2 production from waste activated sludge. Water Research. 2012;46(7):2425-34.
[49] Logan BE. Exoelectrogenic bacteria that power microbial fuel cells. Nature Reviews Microbiology. 2009;7(5):375.

[50] Freguia S, Teh EH, Boon N, Leung KM, Keller J, Rabaey K. Microbial fuel cells operating on mixed fatty acids. Bioresource Technology. 2010;101(4):1233-8.

[51] Aulenta F, Tocca L, Verdini R, Reale P, Majone M. Dechlorination of trichloroethene in a continuous-flow bioelectrochemical reactor: effect of cathode potential on rate, selectivity, and electron transfer mechanisms. Environmental science & technology. 2011;45(19):8444-51.

[52] Aulenta F, Verdini R, Zeppilli M, Zanaroli G, Fava F, Rossetti S, et al. Electrochemical stimulation of microbial cis-dichloroethene (cis-DCE) oxidation by an ethene-assimilating culture. New biotechnology. 2013;30(6):749-55.

[53] Chun CL, Payne RB, Sowers KR, May HD. Electrical stimulation of microbial PCB degradation in sediment. Water research. 2013;47(1):141-52

[54] Pham H, Boon N, Marzorati M, Verstraete W. Enhanced removal of 1, 2-dichloroethane by anodophilic microbial consortia. Water research. 2009;43(11):2936-46

[55] Kannan N, Tanabe S, Tatsukawa R. Toxic potential of non-ortho and mono-ortho coplanar PCBs in commercial PCB preparations:"2, 3, 7, 8-T 4 CDD toxicity equivalence factors approach". Bulletin of environmental contamination and toxicology. 1988;41(2):267-76.

[56] Cao X, Song H-l, Yu C-y, Li X-n. Simultaneous degradation of toxic refractory organic pesticide and bioelectricity generation using a soil microbial fuel cell. Bioresource Technology. 2015;189:87-93

[57] Camacho-Pérez B, Ríos-Leal E, Solorza-Feria O, Vazquez-Landaverde P, Barrera-Cortés J, Ponce-Noyola MT, et al. Preformance of an electrobiochemical slurry reactor for the treatment of a soil contaminated with lindane. JNMES. 2013;16:217-28.

[58] Morris JM, Jin S. Feasibility of using microbial fuel cell technology for bioremediation of hydrocarbons in groundwater. Journal of Environmental Science and Health, Part A. 2007;43(1):18-23.

[59] Morris JM, Jin S, Crimi B, Pruden A. Microbial fuel cell in enhancing anaerobic biodegradation of diesel. Chemical Engineering Journal. 2009;146(2):161-7.

[60] Wang X, Cai Z, Zhou Q, Zhang Z, Chen C. Bioelectrochemical stimulation of petroleum hydrocarbon degradation in saline soil using U‐tube microbial fuel cells. Biotechnology and Bioengineering. 2012;109(2):426-33.

[61] Lin C-W, Wu C-H, Chiu Y-H, Tsai S-L. Effects of different mediators on electricity generation and microbial structure of a toluene powered microbial fuel cell. Fuel. 2014;125:30-5.

[62] Adelaja O, Keshavarz T, Kyazze G. Enhanced biodegradation of phenanthrene using different inoculum types in a microbial fuel cell. Engineering in Life Sciences. 2014;14(2):218-28.

[63] Viggi CC, Matturro B, Frascadore E, Insogna S, Mezzi A, Kaciulis S, et al. Bridging spatially segregated redox zones with a microbial electrochemical snorkel triggers biogeochemical cycles in oil-contaminated River Tyne (UK) sediments. Water research. 2017;127:11-21

[64] Huang D-Y, Zhou S-G, Chen Q, Zhao B, Yuan Y, Zhuang L. Enhanced anaerobic degradation of organic pollutants in a soil microbial fuel cell. Chemical Engineering Journal. 2011;172(2):647-53.

[65] Luo Y, Liu G, Zhang R, Zhang C. Power generation from furfural using the microbial fuel cell. Journal of Power Sources. 2010;195(1):190-4.

[66] Kumar AK, Reddy MV, Chandrasekhar K, Srikanth S, Mohan SV. Endocrine disruptive estrogens role in electron transfer: bio-electrochemical remediation with microbial mediated electrogenesis. Bioresource technology. 2012;104:547-56.

[67] Hunter WJ. Bioremediation of chlorate or perchlorate contaminated water using permeable barriers containing vegetable oil. Current Microbiology. 2002;45(4):287-92

[68] Butler CS, Clauwaert P, Green SJ, Verstraete W, Nerenberg R. Bioelectrochemical perchlorate reduction in a microbial fuel cell. Environmental science & technology. 2010;44(12):4685-91.

[69] Zhao X, Liu H, Li A, Shen Y, Qu J. Bromate removal by electrochemical reduction at boron-doped diamond electrode. Electrochimica Acta. 2012;62:181-4.

[70] Adelaja O, Keshavarz T, Kyazze G. Treatment of phenanthrene and benzene using microbial fuel cells operated continuously for possible in situ and ex situ applications. International Biodeterioration & Biodegradation. 2017;116:91-103.

[71] Thrash JC, Van Trump JI, Weber KA, Miller E, Achenbach LA, Coates JD. Electrochemical stimulation of microbial perchlorate reduction. Environmental science & technology. 2007;41(5):1740-6

[72] Kelly PT, He Z. Nutrients removal and recovery in bioelectrochemical systems: a review. Bioresource technology. 2014;153:351-60.

[73] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. Journal of environmental management. 2011;92(3):407-18

[74] Li Z, Zhang X, Lei L. Electricity production during the treatment of real electroplating wastewater containing Cr^{6+} using microbial fuel cell. Process Biochemistry. 2008;43(12):1352-8.

[75] Heijne AT, Liu F, Weijden Rvd, Weijma J, Buisman CJ, Hamelers HV. Copper recovery combined with electricity production in a microbial fuel cell. Environmental science & technology. 2010;44(11):4376-81.

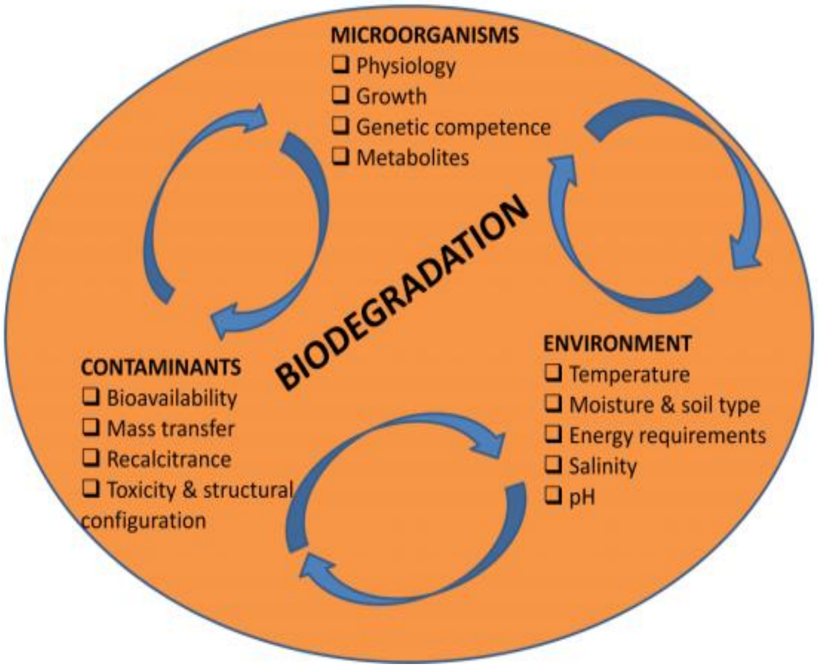

Figure 1. Factors affecting bioremediation of contaminants in the environment (Adelaja., 2015)

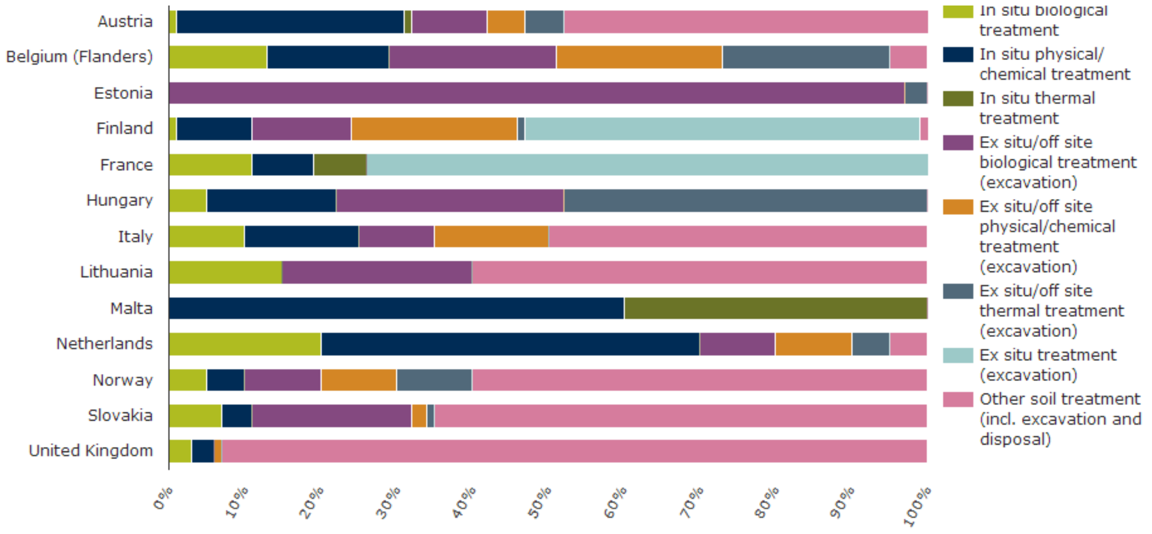

Figure-2. Frequently applied bioremediation techniques in EU countries (European Environment agency, 2018

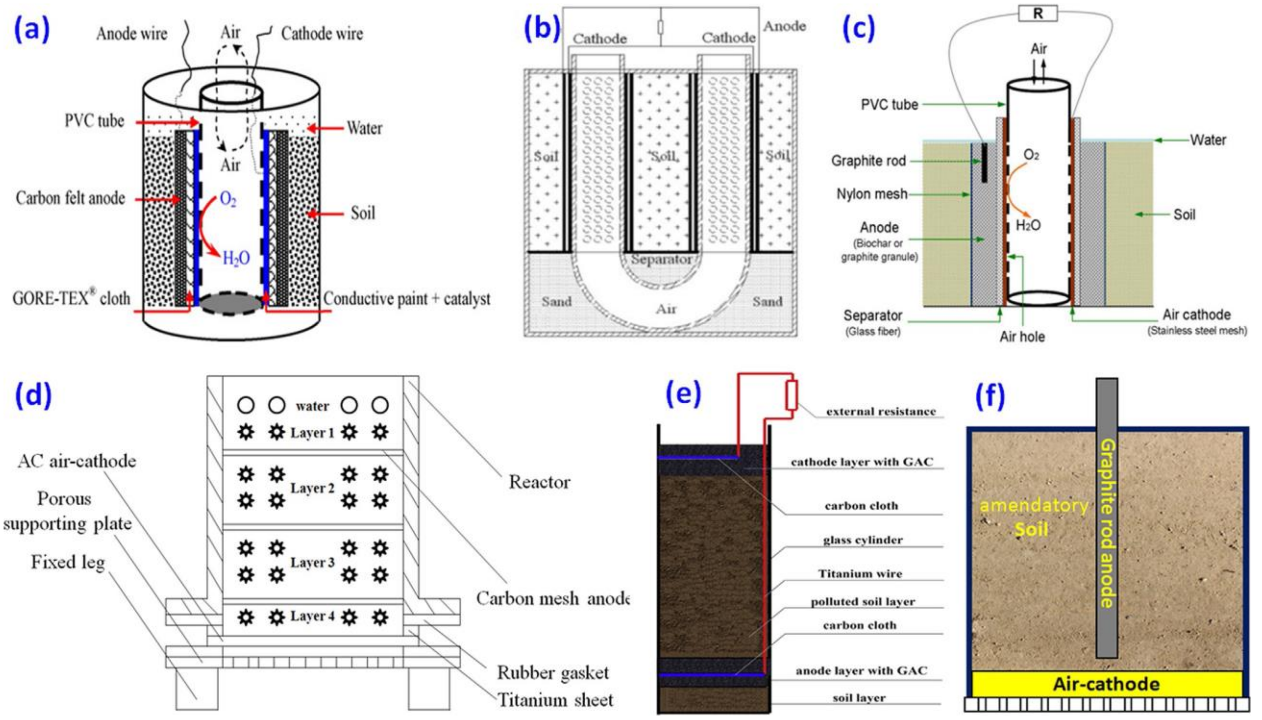

Figure-3: Soil MFC types utilized in remediation of various organic pollutants a) insertion-type, b) U-type, c) column-type, d) multianode, e) topsoil (defined herein); and f) graphite

rod. PVC=polyvinyl chloride, AC=activated carbon, GAC=granular activated carbon (reproduced from Li et al., 2017, with permission)

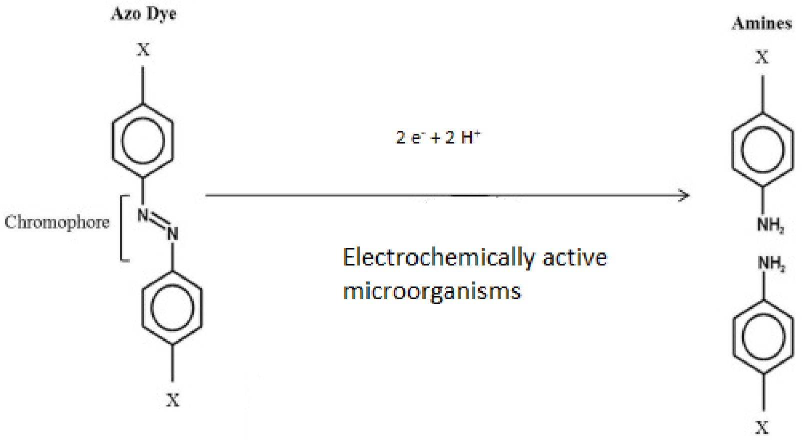

Figure-4: The reductive biotransformation mechanism of azo dye degradation in MFC anodes

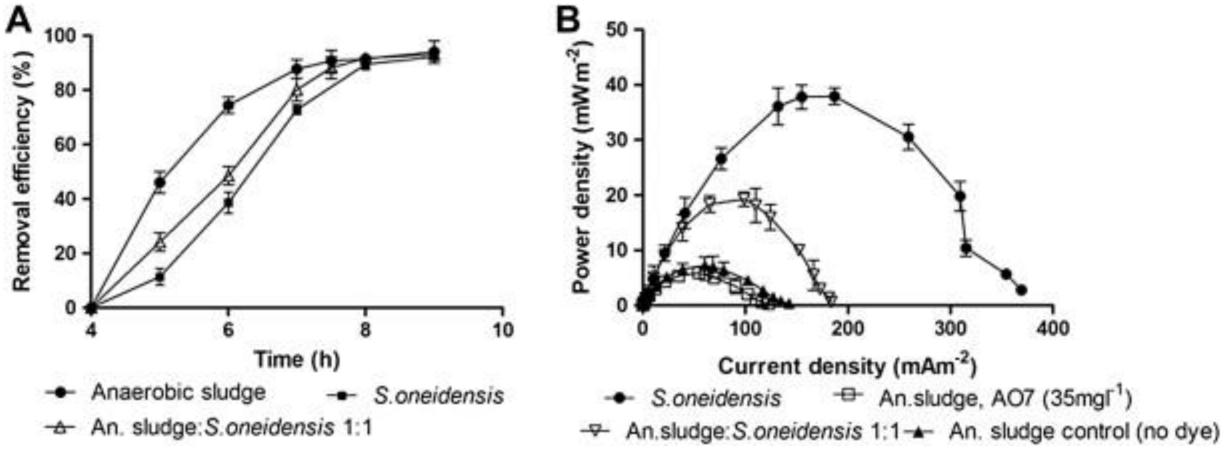

Figure-5: Rapid degradation of the model azo dye AO7 was observed in a study utilizing the electrochemically active microorganism *Shewanella oneidensis* MR-1, in MFC anodes. The high degradation kinetics of AO7 was coupled to biogenic electricity production in the MFC system (reproduced with permission from Fernando et al., 2012).

Figure-6: CNB biotransformation pathway in UASB-BES systems, hypothesized by Jiang et al., 2016 (reproduced with permission from Jiang et al., 2016)

Table – 1: BES studies involving xenobiotic pollutants and the bioelectrochemical characteristics of the BES systems during pollutant remediation

BES type	**Pollutants remediated**	**Inoculum type**	**Power output/consumption**	**Pollutant removal efficiency**	**Reference**
Single-chamber MFC	Brilliant Red X-3B	Mixture of anaerobic and aerobic sludge	275 mW/m^2 power output	>90% over in 50 hours	Sun et al., 2009
Two-chamber MFC	Acid Orange-7	*Shewanella oneidensis* MR-1 and anaerobic sludge	37 mW/m^2 power output	>95% in 30 hours	Fernando et al., 2012
Two-chamber MFC	Mixture of 20 commercial azo dyes	Acclimated anaerobic mixed culture	26 mW/m^2 power output	>90% in 50 hours	Fernando et al., 2013
Constructed wetland coupled-MFC	reactive brilliant red X-3B	Anaerobic sludge	0.8 W/m^3 power output	>95% in 3 days	Fang et al., 2015
Single chamber MFC stacks	Industrial wastewater from leather tanning and wool processing	Acclimated anaerobic mixed culture	55 mW/m^2 power output	>97% in 2 days	Fernando et al., 2016
Microbial electrolysis cell	AO-7 containing synthetic wastewater	Anaerobically digested sludge	0.012 kWh/mol AO-7 power consumption	>80% in 1.4 hours	Mu et al., 2009
Two chamber MFC	2-nitrophenol containing abiotic cathode	*Shewanella decolorationis* S12	1W/m^3 power output	>95% in 30 hours	Feng et al., 2011
UASB coupled BES system	CNB compounds	Anaerobic sludge	1.6 V applied voltage	>95% in five days	Jiang et al., 2016
Soil BES	PCBs and weathered PCB intermediates	Soil microbiota	1.5 – 3.0 V applied voltage	>90% over 10 days	Chun et al., 2009
Two-chamber BES	*cis*-dichloroethene	Activated sludge	Anode polarized at 1V (vs SHE)	7 µmol/L/h	Aulenta et al., 2013
Two-chamber MFCs	Diesel mixtures	Contaminated groundwater from a refinary	31 mW/m^2 power output	>82% removal over 21 days	Morris et al., 2009

U-tube type MFC	PAH compounds	Soil microbiota	0.85 mW/m^2 power output	>95% over 21 days	Wang et al., 2012
Two chamber MFC	Phenanthrene	Co-cultures of *Shewanella oneidensis* and *Pseudomonas aeruginosa*	1.25 mW/m^2 power output	>97% over a week	Oluwaseun et al., 2014
Two chamber MFC	BTEX mixture	Oil cracking wastewater sludge	2.5 mW/m^2 power output	>90% over 65 hours	Lin et al., 2014
Snorkel type MFC	Crude hydrocarbon oil	Sediment microbiota	-	>80% over 460 days	Viggi et al., 2017
Soil MFC	Atrazine	Soil microbiota	66 mA/m^2 current output	>80% over 7 days	Dominguez-Garay et al., 2016
Soil MFC	Phenol	Soil microbiota	29 mW/m^2	>90% over 10 days	Huang et al., 2011
Tubular concentric up-flow MFC	Phenanthrene and benzene in the anode and bromate ions in the cathode	Hydrocarbon acclimated mixed microbial culture	6.5 mW/m^2	>90% hydrocarbon and >79% bromate removal at 10 day HRT	Oluwaseun et al., 2017
Two chamber Bio-electrochemical reactor	Perchlorate ions	*Dechloromonas* spp, *Azospira* spp	Cathode poised at -500 mV (vs Ag/AgCl)	60 mg/L/day removal	Butler et al., 2010 and Thrash et al., 2007
Two chamber MFC	Cr^{6+} ions	Anaerobic sludge	1600 mW/m^2 power output	>99%	Li et al., 2008