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Self-powered, autonomous Biological Oxygen Demand biosensor for online water quality monitoring

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ABSTRACT

Standard Biological Oxygen Demand (BOD) analysis requires 5 days to complete. To date, microbial fuel cell biosensors used as an alternative method for BOD assessment requires external apparatus, which limits their use for on-line monitoring in remote, off-grid locations. In this study, a self-powered, floating biosensor was developed for online water quality monitoring. This approach eliminated the need for external apparatus and maintenance that would otherwise be required by other techniques. The biosensor was able to detect urine in freshwater and turn ON a visual and sound cues (85 dB). The energy needed to operate the biosensor was produced by the system itself with the use of electroactive microorganisms, inside microbial fuel cells. The Chemical Oxygen Demand (COD) was used as a fast method of biosensor validation. When urine concentration exceeded the lower threshold, corresponding to a COD concentration of $57.7 \pm 4.8\ mgO_2\ L^{-1}$, the biosensor turned the alarm ON. The shortest observed actuation time, required to switch ON the alarm was 61 min, when the urine concentration was $149.7 \pm 1.7\ mgO_2\ L^{-1}$. Once the sensor was switched ON, the signal was emitted until the urine organic load decreased to $15.3 \pm 1.9\ mgO_2\ L^{-1}$. When ON, the microbial fuel cell sensor produced a maximum power of 4.3 mW. When switched OFF, the biosensor produced 25.4 μW. The frequency of the signal was proportional to the concentration of urine. The observed frequencies varied between 0.01 and 0.59 Hz. This approach allowed to correlate and quantitatively detect the presence of water contamination, based on signal frequency. The sensor was operating autonomously for 5 months. This is the first report of a self-powered, autonomous device, developed for online water quality monitoring.

1. Introduction

During the past four decades, the quality of surface waters has been changing as the anthropogenic activity has led to a significant increase in organic carbon concentration. Ongoing deposition of hazardous organic substances affects the biodiversity and functioning of aqueous ecosystems [1]. Appropriate steps should be applied to minimise this negative phenomenon, including water quality monitoring. Nevertheless, conventional water quality analysis is often expensive and time consuming, as well being subject to a wide range of complex analytical methods. The majority of these methods can only be conducted offline, in well-equipped laboratories, which make such monitoring difficult in remote areas. An important part of standard water quality analysis is determining the biological oxygen demand (BOD). The principle of BOD analysis has not changed in years, and requires 5 days to be performed. Microbial fuel cell (MFC) biosensors for BOD analysis have been proposed as an alternative approach for water quality monitoring [2], although the principle has been known for almost forty years [3]. MFC biosensors, similarly as the bioreactor-based biosensors, offer the advantage of online monitoring of the biological processes and corresponding BOD [4].

A microbial fuel cell is a biological energy transducer, in which electroactive microorganisms oxidise the organic substrates and use the electrode as a terminal acceptor of electrons. In conventional single chamber MFCs, the anode is separated from the cathode by a semi-permeable membrane, which allows the transport of cations. When the external load is applied, protons and electrons combine at the cathode, which is exposed to free air, to form water. Electrical current is the by-product of biochemical oxidation of the substrate fed to the microbes in the anode [5]. Several approaches have been used to improve the performance of MFCs,

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including the use of novel, advanced materials [6,7]. On the other hand, the use of ceramic separators as membranes reported in 2010 [8], has reduced the main MFC costs significantly (as low as 4.14 GBP m^{-2} [9]) since it is used as both the membrane and structural material at the same time, to, -making MFC – based technologies accessible to countries of the Developing World [10]. Moreover, the MFC technology is known for the reconfigurability of its components, that makes many practical applications possible [11].

Electricity generated in MFCs can be directly correlated with the concentration of bioavailable organic matter. Moreover, the response time of such biosensors is significantly lower, in comparison to conventional techniques. Response times in the range of minutes have been reported in the literature [12]. In a study reported by Di Lorenzo et al. [13] the response time, defined as time needed to reach 95% of the steady current, was as low as 2.8 min. The mixed bacterial populations are able to utilise a wide range of substrates, including urine [14]. Recently, MFC-based biosensors were also studied for the use in toxicity monitoring. It was shown, that the power output can be adversely correlated with the presence of organic and inorganic toxicants [15]. The sensitivity of such sensors was demonstrated for several toxic metals: when Cd^{2+} ions (0.1–100 $\mu g\,L^{-1}$) were introduced to such sensor, the response time was 12 min [13]. In another study, Stein et al. demonstrated the sensitivity of a MFC biosensor against Ni ions equal to 0.0027 $A\,m^{-2}\,mg^{-1}\,L^{-1}$ [16]. Nevertheless, MFCs are highly dynamic systems and a number of factors can influence their output signals and hence the direct "readings". Some of these are temperature, pH and conductivity, which can affect power output and therefore signal accuracy. Several approaches have been taken to improve the correlation of MFC readings with BOD concentration and in some of these studies a determination coefficient of as high as 0.99, has been reported [17,18]. It was also shown, that qualitative data can be extracted from the MFC output by using artificial neural networks, to identify the compounds that can be found in wastewater [19].

Although MFC biosensors offer the advantage of correlating biological activity of electroactive microorganisms with the chemical composition of the feedstock, they still require an external data logging apparatus. So far, the family of self-powered biosensors contains solutions, in which the term "self-powered" is rather referring to producing current *in situ* as a result of the reaction, but not necessarily using this generated current to power the biosensor itself [20]. For example, engineered *P. aeruginosa* cells were capable of synthesising redox mediators for current generation as a response to the presence of homoserine-lactones, and the logging of the biosensor response was performed by the external apparatus. The field of self-powered devices is currently being developed for systems consisting of flexible piezo-electric energy harvesters (nanogenerators) and these devices are mainly developed for implantable electronics in healthcare [21,22]. An interesting approach for a self-powered device, was reported by Zloczewska et al. [23], who developed the electrochromic biosensor. The quantitative information was provided by the colour change of the prussian blue dye, as a result of current generation. Another interesting example of a self-powered biosensor, involved an enzymatic biofuel cell as the biological actuator. The biosensor proposed by Miyake et al. [24] was able to convert simple sugars like glucose or fructose into usable amounts of energy, that could be spent to power an LED diode, and the authors demonstrated its use in real biological fluids. Furthermore, it was recently shown, that a biofuel cell operating in fruit was able to produce 0.670 mW of power which was sufficient to transmit the radio signal for at least 6 h [25]. Enzymatic biosensors offer a great advantage of substrate specificity and the potential for application in monitoring sugar levels in biological tissue as well as giving relatively high power performance. They can also be integrated into high-throughput platforms, as recently demonstrated [26]. Nevertheless, the applicability of enzyme-based fuel cells for long-term online monitoring has never been demonstrated, due to the limitations of the enzyme lifetime, which varies from days to weeks [27]. Although this offers great potential in biological or food samples, the need for regenerating the enzyme(s) bound to the electrode surface makes such biosensors unsuitable for autonomous long-term operation in real environmental conditions, such as online water monitoring. In contrast, MFC biosensors are able to respond to a wide range of chemicals, offering lower substrate specificity. The bacteria present on the electrodes are able to reproduce and hence maintain the sensor's sensitivity. Self-sustainable operation of a biosensor would offer the advantage of interpreting the sensor measurements without the need for any external power source and peripheral instrumentation.

The aim of this study was to build an autonomous, low-cost, off-grid device that would be able to detect organic contaminants, such as urine, in freshwater, and indicate their presence by emitting audio and visual signals to the surrounding environment.

2. Materials and methods

2.1. Biosensor construction

The biosensor was built using four, single chamber MFCs, electrically connected in parallel, and each MFC was made from terracotta cylinders. The ceramic cylinders served as both the cation exchange membrane and the chassis of the MFC. Each cylinder was 150 mm long, with an internal diameter of 42 mm and external diameter of 48 mm. The anode was built from carbon fibre veil with a carbon loading of 30 $g\,m^{-2}$ (PRF Composite Materials, UK). Carbon veil was cut into rectangles of 1250 cm^2 total macro surface area, folded, and wrapped around the cylinder. Plain nickel-chromium wire (Ni-Cr, 0.45 mm, Scientific Wire Company, UK) was used as the current collector and to hold the carbon veil in place. The cathode electrodes were prepared as described by Gajda et al., 2015. In brief, carbon veil was coated with a mixture of PTFE (Sigma Aldrich, UK) and activated carbon powder (G. Baldwin and Co., UK). The rectangular cathode pieces were folded and placed inside the cylinders. The hydrophobic carbon fibre veil side was exposed to air, whilst the activated carbon layer was directly in contact with the ceramic membrane. The total surface area of the cathode was 180 cm^2 and the obtained carbon loading was approximately 60 $mg\,cm^{-2}$. Such a configuration prevents the biofouling of the cathode [29].

The MFCs were attached to 3 mm thick acrylic plates and held in place by O-rings made out of rubber. Polystyrene blocks were attached to the external part of the acrylic plate, in order to allow the ceramic cylinders to be submerged in water, but leaving the top of the MFC biosensor exposed to air, when floating (Fig. 1).

The output from the four MFCs was connected to an energy management system (EMS), which consisted of: (i) energy harvester (BQ25504, Texas Instruments, USA) supplied with a variable resistor to control the maximum power point tracking (MPPT) feature; (ii) a super-capacitor and (iii) a hysteresis board. For the first 5 days of operation, a 3 F super-capacitor was used. Then, the super-capacitor was replaced by a 6800 μF capacitor until the 11th day, following which a 120 μF was connected. The hysteresis board consisted of a comparator, which allowed the super-capacitor to discharge when the voltage reached 3.1 V, and then to charge, when the voltage was down to 2.3 V. Additionally, for the period of time when the 6800 μF capacitor was connected, a comparator operating between 2.8–2.9 V was used. A red LED diode and a buzzer were connected in parallel, representing the external load. The power consumption of this load was measured prior to starting the