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Bioenergy from wastewater in a microbially-charged redox flow cell

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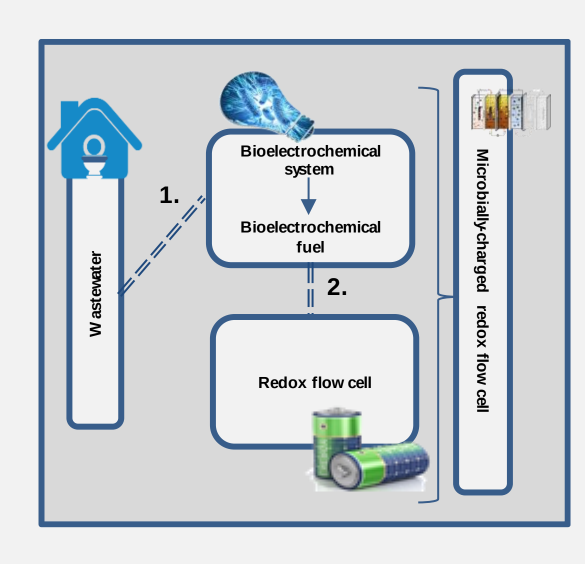

Wastewater is a valuable renewable energy source to generate newest approaches for electrochemical energy conversion in bioelectrochemical system (BES) for energy storage devices. A BES to generate a bio-charging redox pair to be use as negalyte in a redox flow cell (RFC) was study. In BES 2,6-antraquinone was introduced as new redox pair (catholyte), where wastewater mixed communities were the anolyte for the generation of a bio-charged redox pair. The BES results indicated the reduction of the quinone (*ca.* 50 %), promoting power density *ca.* 10 mW m^{-2}. A RFC with the bio-charged redox pair as negalyte and potassium hexacyanoferrate (III) as posilyte was tested, reaching *ca.* 100 % of coulombic efficiency, with potential and energy efficiencies *ca.* 60 %. Wastewater in the new microbially-charged redox flow cell generate a clean energy that can be stored in a new landmark system.

Redox flow batteries (RFB) are electrochemical energy storage devices where the energy is stored in the redox pairs dissolve in a aqueous solution of supporting electrolyte [1]. Several works describing different types of redox pairs in aqueous supporting electrolyte solutions are well-known. Organic redox species, such as anthraquinones were a step forward for use in RFB, been projected as promising for their low cost and lower toxicity substituting ion metals as redox pairs. [2]. RFB exploring solar energy as renewable energy source was designed in a solar redox flow cell [3]. In these systems solar energy is converted into storable electrochemical fuels. These advance open doors for new ways to store energy and coupling processes with RFB.

Wastewaters are an attractive source of organic compounds, been an accessible and low cost renewable energy source for the recovery of different biochemical products, such as scarce metals, methane or hydrogen and their use for bioenergy production [4]. Bioelectrochemical systems (BES) are innovative microbial technologies that are commonly used for applications in wastewater treatment, nutrients recovery, biosensing, bioremediation and renewable energy generation [5]. BES are not yet able to reach the same maximum power densities as an RFB and BES electrochemical energy generated is not safeguarded in the system.

The purpose of this work is to harnessing wastewater for bioenergy storage in a microbially-charged redox flow cell, assessing their capacity to produce storable electrochemical fuels in BES, which can be used to produce electricity in a redox flow cell (as shown in the Graphical Abstract). The 2,6-anthraquinone was the redox chemical specie used in the BES as catholyte for their electrochemical reduction with wastewater (anolyte). The BES were operated with an external resistance (1000 Ω) in batch conditions, the potential was measured over time. In a second step, a redox flow cell (RFC) was using, with potassium hexacyanoferrate (III) as posilyte and as the negalyte the 2,6-anthraquinone charged by the BES.

The results from the BES pointed that the electrochemical reduction of 20 mM 2,6-AQDS (50 cm^3) in BES with wastewater mixed communities was observed after 27 days, fact assessed by a visually distinctive color change (from yellow to dark red), characteristic of the 2,6-AQDS. UV-Vis spectrophotometry at 330 nm allowing estimating the electrochemical conversion of the quinone, which was approximately 50 %.

The BES maximum power density was *ca.* 10 mW·m^{-2} at 80-100 mA·cm^{-2} and display *ca.* 40 % of coulombic efficiency. The maximum power density and coloumbic efficiency were obtained with wastewater mixed communities and complex carbon sources are in the range of previous reports with BES operated with wastewater [6], [7].

The RFC operated over time with a constant current density of 3.75 mA·cm^{-2} for 10 cycles resulted in *ca.* 100 % coulombic efficiency and *ca.* 60 % potential efficiency and *ca.* 60 % energy efficiency. The RFC promoted similar result efficiencies to previous works [8].

Conclusions

In this study the wastewater potential as renewable energy source to convert into storable electrochemical fuels was assessed, and the bio-charged redox pair was tested in a redox flow cell (2,6-AQDS || $[Fe(CN)_6]^{4-}$) with *ca.* 100 % coulombic efficiency. The integration of the BES and a RFC resulted in a half microbially-charged redox flow cell that is a novel promising approach of converting wastes into storable and easy to use green energy and a way to promote circular economy.

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