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Agro-food industry wastewater treatment with microbial fuel cells: Energetic recovery issues

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ABSTRACT

Wastewater treatment, necessary for the preservation of water and environmental quality, usually requires considerable energy inputs to obtain desired targets. New paradigms of circular economy require that new technological approaches for energy and resource recovery should be implemented in lieu of traditional, energy-hungry technologies. Microbial fuel cells represent an eco-innovative technology for energy and resources recovery from a variety of wastewaters. Agrofood wastes are specially indicated due to their high biodegradability. The current research was conducted to: assess bioelectrochemical treatability of dairy wastewater by MFCs, determine operational effects on MFCs electrical performance and evaluate possible strategies to reduce overpotentials. For this purpose, two parallel MFC reactors were continuously operated for 2.5 months, fed with undiluted dairy wastewater. The study demonstrated that these types of industrial effluents can be treated by MFCs with high organic matter removal, recovering a maximum power density of over 27 W/m^3. Achieved results were better than previous MFC-experiences dealing with dairy (and other types of) wastewater treatment, and show that recovery of energy from treatment of organic wastes is a feasible strategy on the pursuit of sustainable technologies.

Introduction

Wastewater treatment, necessary for the preservation of water and environmental quality, usually requires considerable energy inputs to obtain desired purification targets. On average, the energetic consumption of wastewater treatment with conventional processes is about 0.2–0.8 kWh/m^3, depending on various factors, including wastewater and process type. In case of aerobic processes, the energy used for mixed liquor aeration (oxygenation) alone can amount to more than 50% of the total energy used by the treatment facility [1]. New wastewater cycle paradigms [2,3] suggest that new technological approaches for energy and resource recovery should be implemented *in lieu* of traditional, energy-hungry technologies, such as the standard Activated Sludge (AS) process and its modifications (including membrane bioreactors, MBRs). The agro-food industry, in particular, produces massive amounts of organic materials as secondary waste streams that could be tapped for energy recovery and resources [4]. Several alternative processes have been proposed, including Granular Activated Sludge (GAS) in the aerobic processes realm, and Upflow Anaerobic Sludge Blanket (UASB) in the anaerobic one. The former allows considerable energy savings (not to mention footprint and volumetric

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reduction) compared to traditional AS processes [5], while the latter would reduce energy consumption to the bare minimum necessary for wastewater circulation and allow recovery of a mixture of biogas, largely composed by methane [6].

Microbial electrochemical systems (MESs), also appear to provide a potentially attractive alternative to wastewater treatment processes with energetic recovery, within the current global economic framework. In MESs, like microbial fuel cells (MFCs), electroactive bacterial species (EABs) rely on the same substances used in anaerobic biodegradation to transfer electrons and directly produce current from the chemical energy, contained in an organic biodegradable substrate [7].

In MFCs, EABs catalyse (one or both) oxidation and reduction reactions, each occurring in a separate chamber (anode and cathode) and containing the respective electrodes, connected by an external electrical circuit. Internally, the chambers are separated by a selective ionic exchange membrane (IEM), so that electrons and protons released by the bacteria while degrading the substrate at the anode can travel towards the cathode, where they combine with the terminal electron acceptor of the reaction (usually, oxygen) [8,9]. Advantages characterizing MFC processes, compared with other state-of-the-art wastewater treatment processes are several: first, these processes happen to be extremely versatile in reference to treatable substrates. Experiences have been reported in literature with simple liquid substrates, such as glucose [10], volatile fatty acids [11] and alcohols [12], as well as with complex mixtures, such as domestic wastewater [13,14], brewery [15], dairy [16–18], winery [19,20], soybean edible oil refinery [21], distillery [22], food-processing effluents [23]. Even when used to treat landfill leachate (usually considered somewhat refractory to biological treatment), reported organic removal rates reached 7 kg COD (Chemical Oxygen demand)/m^3 d [24,25], better than standard aerobic processes (0.5–2 kg COD/m^3 d), and in line with those of anaerobic digestion (8–20 kg COD/m^3 d). MFCs have been reported being able also to remove (partially or completely) pharmaceutically active compounds from wastewater [26]. MFC applications to the degradation and energy recovery from solid food industry waste have also been reported recently [27]. Additional, non-negligible advantages over other biological processes are low biofilm yield, possibility to operate at low temperatures, strong reduction of aeration needs (only supplied as electron acceptor at the cathode in dual cell systems only), direct electricity production.

MFCs, however, are still characterized by some drawbacks, including low specific electric production (10–100 W/m^3 of total reactor), that are still limiting the industrial applicability of this technology [28]. Attempts of MFCs electric optimization include development of non-Platinum-group catalysers for oxygen reducing cathodes [29], morphologic modification of the electrodes and combination of different electrode materials [30–32], development of biocathodes [33], hydraulic and electric stacking of several MFC units [34], tracking methods for the optimal external resistance [35].

Utilization of agrofood substrates (swine manure, brewery, dairy or winery effluents) is particularly promising for MFCs industrialization, given their high organic content (COD values can go up to 10 g/L) and biodegradability (generally BOD/COD ratio is higher than 60%) [36,37]. However, treatment of complex substrates increases bacterial community complexity, and this can lead to unexpected interrelated connections between microbial species [38]. The anode chamber anaerobic condition may induce unwanted side-reactions such as methanogenesis, which directly competes with electric current production, or heterotrophic denitrification [39]. It was demonstrated that high fermented substrates concentrations favour methanogenic activity against exo-electrogenesis, reducing MFCs' electrical efficiency [40].

Dairy industry occupies one of the leading positions in the Italian agro-food sector (Italy also produces 6% of the world's cheese production). In industrial cheese-making processes, about 2–4 L of wastewater are produced per L of processed milk [41], with qualitative characteristics summarized in Table 1. The organic fraction consists usually of easily biodegradable organic substrates (lactose), with the presence of some slowly biodegradable lipids and proteins [42]. Nitrogen is mainly present in organic form, bonded in milk proteins, while phosphorous is mainly in orthophosphate form. Detergents and additives used in industrial and cleaning processes can significantly affect pH and alkalinity of wastewater.

Bioelectrochemical recovery of electricity from dairy wastewater with MFCs has been previously investigated in recent years, as summarized in Table 2. Single chamber, dual-chamber, and tubular MFCs have been tested, with electrodes of different materials including carbon, graphite, stainless steel or composites. The highest reported power density (20.2 W/m^3) so far was achieved by Mardanpour et al. [45], using a tubular MFC equipped with a 0.5 mg Pt cm^{-2} catalyst load on the cathode. Other studies demonstrated that cathode catalysts may be avoided, without negative effects on organic matter removal efficiency, but with considerable reduction of power density (90% lower) and Coulombic Efficiency (CE, 44% lower) [46,47]. Experiences of continuous-fed MFCs treating dairy wastewaters achieved mixed results [17,18].

Despite all the promising results obtained mostly in short-term studies (1 month maximum duration), MFCs scientific literature is still lacking comparative long-term studies related to dairy wastewater treatment in continuous conditions. Molognoni et al. [18] had previously tested a single MFC reactor for dairy wastewater treatment, achieving encouraging results. Before an attempt at system upscaling,

Table 1 – Physico chemical characterization of wastewater effluents produced in a cheese factory. (Concentration ranges elaborated from Refs. [41,43,44]).

Parameter	Unit	Concentration range
Total Suspended Solids (TSS)	mg TSS/L	250–2700
Chemical Oxygen Demand (COD)	mg O_2/L	650–3000
Biological Oxygen Demand (BOD_5)	mg O_2/L	300–1400
Organic nitrogen (N_{org})	mg N/L	10–140
Ammonium nitrogen (N–NH_4)	mg N/L	10–20
Nitrates (N–NO_3)	mg N/L	10–20
Phosphate (P)	mg P_2O_5/L	10–130
Chlorides (Cl)	mg Cl/L	50–500
pH (–)	pH units	4–12
Alkalinity (HCO_3)	mg HCO_3/L	250–650

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