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Microbial electrochemical fluidized bed reactor (ME-FBR): An energy-efficient advanced solution for treating real brewery wastewater with different initial organic loading rates.

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ABSTRACT

Electroactive bacteria are able to evolve strategies to transfer electrons with electroconductive materials. The boundaries of using electroactive bacteria to scale up wastewater treatments indicate the necessity to evaluate some of the most critical design and operational aspects. In this context, we have explored a concept so-called microbial electrochemical fluidized bed reactor (ME-FBR) for optimizing treatment of brewery wastewater by evaluating the anode potential, from + 200 mV to + 800 mV (vs. Ag/AgCl, 3 M reference electrode), in a vast range of Organic Loading Rate (OLR;0.23 kg COD/m^3 d^{-1} to 23.60 kg COD/m^3 d^{-1}). Furthermore, the impact of the cathode nature (stainless steel mesh and sponge) and the electroconductive bed volume was evaluated regarding the wastewater treatment capacity. This manuscript reveals a positive impact on the ME-FBR capacity for treating wastewater: COD removal (87%) and nutrient removal (66% of TN and 75% of TP). Finally, the treatment energy consumption was always under 0.4 kWh Kg $COD_{removed}^{-1}$ which was 10-fold lower than the required energy for aerating bioreactors from conventional activated sludge or membrane reactors.

1. Introduction

Microbial electrochemical technologies (MET) have gained attention in the last years due to the capacity of living microorganisms to couple their metabolism to electrodes. The released electrons from the organic matter oxidation are transferred to electroconductive electrodes acting as a terminal electron acceptor (TEA), replacing the aeration step from conventional aerobic reactors where oxygen is the main TEA [1–4]. Those microorganisms, so-called electroactive bacteria [5–7], have been widely studied for different applications where MET has been positioned as a promising novel technology. Some of those technologies are referred to wastewater treatments [8–11], synthesis of organic compounds [12,13], development of biosensors [14–16], and removal of recalcitrant pollutants [17–20]. Nevertheless, the main studies related to MET have been performed at a labscale, achieving remarkable results to overcome current problems related to the most common biological treatments installed and operated at an industrial scale [21,22]. However, the upscaling of these technologies is the most critical bottleneck that has been faced [23–26]. Besides the wide application and expected potential of MET, such technologies have not been entirely explored and understood, so further research should be done to achieve the final commercialization as electrochemical systems. The main problems that directly affect the scale-up of these technologies are related to abiotic factors. Some of those abiotic factors are i) the nature of the electroconductive materials and ii) geometries to enhance the MET performance at pilot, pre-industrial, and industrial scale. In addition, some construction costs (CAPEX) like electrode materials or membranes have also become essential by making MET less competitive against traditional technologies [27–31].

The wastewater treatment capacity of METs has been historically evaluated through three different configurations (i) microbial fuel cells (MFC), (ii) microbial electrolysis cells (MEC), and (iii) microbial electrochemical snorkel (MES). Usually, MFCs have been designed according to the capacity for generating electrical power during the

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wastewater treatment [32–36]. Furthermore, MFC has also been operated to internally convert the generated power in desalination [36–38]. On the other hand, MECs have been generally assessed to develop new and innovative remediation processes, such as dechlorination [38–40], or improve the production of volatile fatty acids from CO_2 [39–41]. Nevertheless, the high capacity of MEC to improve the wastewater treatment capacity by applying a very low potential drop between the anode and a reference electrode has not been deeply assessed at a large-scale [42]. In this context, optimization of anodic stimulation to catalyze the organic matter oxidation could be a first step towards the final development of the bioelectrochemical technology at industrial scale. So far, only hybrid concepts where MET are integrated into constructed wetlands (CW) had been extensively studied and scaled up to full scale (ca. 100 m^3/day). Such solutions, so-called METland®, are equipped with fixed-bed biofilters made of electro-conductive coke or biochar [43], rather than the installation of electrical circuits generally used in conventional METs. They were initially anoxically operated under snorkel configuration [44,45], where electron flow along the electroconductive bed was demonstrated by measuring the electric potential [45,46]. More recently, METland® shas been designed to control the electron flow towards specific bed areas [47] or even operate in the presence of oxygen for enhancing nitrification reactions [48]. The high capacity of electroactive bacteria to transfer electrons to the electroconductive material boosts the organic matter consumption contained in real wastewaters, resulting in a sustainable solution according to LCA analysis [49].

Thus, electrode materials (working and counter electrodes) have been under discussion during the last decades since redox reactions occur over the electrode surfaces [50]. Nevertheless, not only the electrode material of the counter electrode (usually the cathode in most MET-based wastewater treatments) but also its geometry should be deeply studied to reduce as much as possible the undesirable higher overpotentials leading to high power consumptions [51–53]. In this context, alternative METs have outstanding potential but are less developed and required in-depth research to scale up the technologies. This is the case of microbial electrochemical- fluidized bed reactors (ME-FBR), a system representing a new paradigm where bacteria interact with fluid-like electrodes [54] instead of classical materials like graphite plates or carbon felts. The evaluation of such electroconductive bed materials as working electrodes is gaining interest due to the high mass transfer area leading to stimulate both anodic oxidative reactions [7,54] and cathodic reductions like denitrification [55]. Furthermore, such fluid-like materials show a higher active surface area, which can further reduce the operative costs of this technology [4,56]. Another strategy for using a mobile 3D-electrode configuration is the use of carbon-based capacitive mobile granules. These granules are covered by an electroactive biofilm that transfer the electrons resulting from its metabolism to the conductive material. Afterwards, the charged granules are recirculated to the anodic chamber of an external MFC and transfer the electrons to a current collector [57], remaining oxidized and acting as an electron sink again.

In this context our study shows a comprehensive evaluation and optimization of the main bioelectrochemical elements of a microbial electrochemical fluidized bed reactor (ME-FBR), (i) the influence of anodic potential for treating real brewery wastewater, (ii) the impact of two different stainless steel (SS) electrodes on the electrochemical overpotential and (iii) the correlation between the electroconductive bed volume and the removal of COD and nutrients.

2. Materials and methods

2.1. ME-FBR design, construction, and operation

The ME-FBR was designed as previously described [7,54,58]. The tubular ME-FBR had a total volume of 1.2 L, including the recirculation pipe and the electroconductive bed volume (Fig. 1). The working

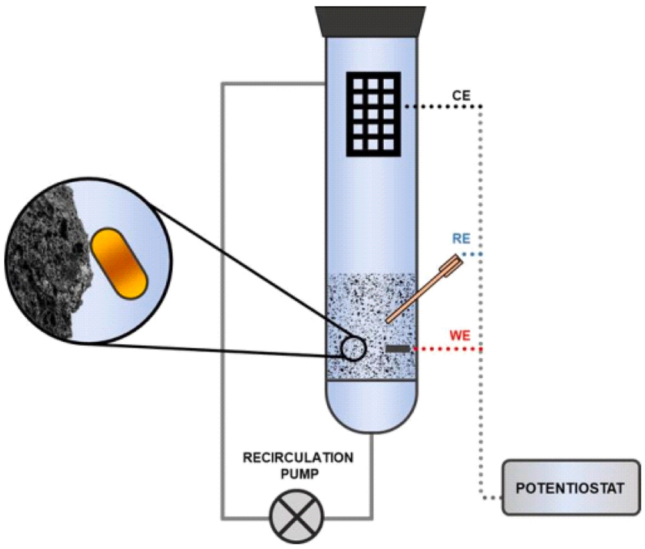

Fig. 1. ME-FBR diagram.

fluidized electrode (anode) consisted of an electroconductive bed composed of activated carbon particles with a diameter range of 0.6–1 mm (Chemviron Carbon®, Belgium). A graphite plate (20 ×80 mm) was vertically immersed into the electroconductive bed material, acting as current collector accepting the electrons from the charged fluidized electrode. Four electroconductive bed volumes were evaluated in relation to the reactor volume (5%, 10%, 20%, and 30% $V_{EC\ bed}/V_{reactor}$). The counter electrode was made up of stainless steel and placed at the top of the column. Two different geometries were evaluated to evaluate the overpotential related to each configuration. The first configuration was a SS mesh (20 ×80 mm; PAMEX®, Spain), while the second one was a SS sponge (40 ×150 mm; PAMEX®, Spain). In order to get relevant data related to the electrochemical performance of both counter electrode geometries, anode potential, cathode potential, and cell potential were measured three times a day, during seven days. During the anode polarization test, the SS mesh was equipped in the ME-FBR. This SS mesh was replaced by the SS sponge during the electroconductive bed volumes experiment attending to the obtained results.

The ME-FBR was operated as a three-electrode electrochemical cell, and the fluidized bed potential was fixed to different values (all potentials are reported versus Ag/AgCl electrode). An Ag/AgCl 3 M KCl electrode (HANNA) was used as a reference electrode. The potentiostat used was a NEV3 Nanoelectra (Spain). The data logger installed in the NEV3 potentiostat registered the output current during the wastewater treatment. Such electric current was further normalized with the anode volume area to obtain the current density of the process.

2.2. Hydraulic operation of ME-FBR

Bed fluidization was achieved by a medium recirculation (0.68 cm s^{-1}) from the top reactor section using a peristaltic pump (Heidolph 5006, Germany). Furthermore, a peristaltic pump (Watson-Marlow 205 S) was used to continuously feed wastewater into the ME-FBR at a level over the fluidized bed. In order to mimic the hydraulic retention time (HRT) from brewery WWTP, we performed all experiments at 12 h HRT.

2.3. Inoculum, wastewater description, and chemical analysis

Activated anaerobic granular sludge (5 mL) from Mahou-San Miguel Company, a brewery plant in Alovera (Guadalajara, Spain) was used as inoculum for the microbial electrochemical treatment.

The wastewater was also collected from the brewery plant. Such

wastewater was previously pre-treated through a coagulation step followed by a post-treatment pH adjustment in the brewery plant. Inlet wastewater and effluent samples were daily taken and stored (−20 ºC) till analysis. Table 1.

Chemical Oxygen Demand (COD) was measured with a commercial kit from HACH (Germany) by adding 3 mL of the sample. The sample tubes were digested for 2 h at 148 ºC in a HACH DRB200® thermoreactor and determined by a HACH DR1900® spectrophotometer. For the determination of nutrients, HACH cube tests were also used following the instructions described by the manufacturer. All the equipment was portable since tests were in situ performed in the brewery WWTP. During the experiments, pH and conductivity were also measured with a multiparametric probe HACH HQ30D.

3. Results and discussion

The electrochemical performance of Microbial electrochemical fluidized bioreactors (ME-FBR) has been explored as technological solution for removing organic pollutants and nutrients from a real brewery effluent.

3.1. ME-FBR for removing organic pollutants

Wastewaters from the brewery industry are readily biodegradable ($BOD_5/COD>0.5$) characterized by containing high content of non-toxic volatile fatty acids (VFA), carbohydrates, and proteins, all suitable for biological treatments [59]. In this context, the treatment capacity of ME-FBR has been tested under a vast range of (i) organic loading rates (OLR: 0.24–23.60 kg COD m^{-3} d^{-1}), and (ii) anode potential (+200 mV to + 800 mV vs Ag/Ag/Cl).

Three different stages were observed regarding the assessment of OLR and anode potential in terms of COD removal. A first stage was observed when the system was operated at low organic loads (< 0.8 kg COD m^{-3} d^{-1}). Under this scenario, the COD removal was in a similar range (70–75%) (Fig. 2.a). A second stage was clearly observed when the system was operated at medium organic loads, between 1.15 and 3.8 kg COD m^{-3} d^{-1}. Indeed, higher COD removals were achieved at low anode potentials (79% COD removal at +200 mV anode potential).

Nevertheless, organic matter concentration was no longer a limitation at this organic load range, so a remarkable increment in COD removal was observed by applying higher anode potentials [60]. For example, a COD consumption above 90% was achieved at + 600 mV (vs. Ag/AgCl) anode potential, representing an increase of 10% in the treatment capacity by only upgrading the applied anode potential. However, during the third stage, the main differences were observed when the ME-FBR was operated at OLR values beyond 3.8 kg COD m^{-3} d^{-1}. In this scenario, it was clearly observed a linear growth between the COD consumption and the anode potential. Actually, a net improvement of ca. 40% in COD removal was reported just shifting from + 200 mV to + 800 mV (vs. Ag/AgCl, 3 M reference electrode). This ME-FBR behavior reflects the direct influence of the set anode potential on COD removal when organic matter concentration was not a limitation during the wastewater treatment.

This result demonstrates that the high versatility and COD removal capacity of ME-FBR (above 90% COD removal at +600 mV) represents a crucial opportunity to outcompete with other well-established solutions as membrane bioreactors (MBR) [61], upflow anaerobic sludge blanket reactors (UASB) [62,63] and sequencing batch reactors (SBR) [64] where COD removals values from brewery wastewater are in a 70–80% range.

Table 1
Chemical and physical parameters of the brewery wastewater (inlet stream).

Parameter	Brewery wastewater
pH	2.7 ± 0.5
Conductivity (mS cm^{-2})	2.7 ± 0.2
COD (mg L^{-1})	2947 ± 139
Total nitrogen (mg L^{-1})	58.2 ± 11.2
Total phosphorous (mg L^{-1})	17.2 ± 2.1

The produced current density was also evaluated during the operation of the ME-FBR (Fig. 2.b). Relevant information about the dependency of the electroactive bacteria with the available organic matter can be observed in such assay. Two different scenarios (Fig. 2.b) can be observed regarding current production. The first one, with a range between 0.24 and 1.73 kg COD m^{-3} d^{-1}, the current density increased as OLR was enhanced, achieving the maximum value at 0.62 kg COD m^{-3} d^{-1}, with a current density of 180 A m^{-3}. This exponential growth of the current density was directly related to the higher COD consumption rate of the ME-FBR (Fig. 2.a). Furthermore, the Monod shape (from 0.24 to 1.73 kg COD m^{-3} d^{-1}) shown in the range of OLR reflected an optimal behavior of electroactive bacteria was obtained when the ME-FBR was operated in an OLR range between 0.62 and 1.73 kg COD m^{-3} d^{-1}. This reason is consistent, attending to the maximum obtained current density in that range, which was pretty stable, also showing the robustness of the ME-FBR in the long-term operation.

The second scenario was observed for OLR beyond 1.73 kg COD m^{-3} d^{-1}. Such high OLR led to a rapid decrease in the current density suggesting some kind of inhibition for the microbial electron transfer to the electrode. Nevertheless, the complete inhibition of alternative non-electroactive bacterial consortium did not occur, attending to the high COD removal value (Fig. 2.a). This behavior can be explained according to the electrochemical stimulation of other microbial metabolisms, as fermenting microorganisms or methanogens, where the terminal electron acceptor is not necessarily the electrode [7,65].

3.2. Impact of bed volume on ME-FBR efficiency

The electroconductive bed material is effectively acting as electron acceptor for electroactive bacteria growing in ME-FBR. However, due to the energy investment in bed recirculation and operation-based bed replacement, the required volume of fluidized material will have a remarkable technical and economic impact on this technology. Indeed, it should be minimized while keeping optimal biodegradation capacity.

COD removal and current density were monitored as main parameters to evaluate the influence of the volume of the electroconductive bed (initial electroconductive bed volume versus the reactor working volume, $\%V_{EC\ bed}/V_{reactor}$). Four different fluidized anodes were studied, from 5% to 30%$V_{EC\ bed}/V_{reactor}$ with an OLR of 1.73 kg COD m^{-3} d^{-1}. Our results revealed a direct correlation between the volume of the fluidized anode and the treatment capacity. So, a bed volume increment from 5% to 10% resulted in up to a 22% increase in COD removal. Furthermore, the current density was also enhanced from 0.25 A m^{-3} to 8.60 A m^{-3}. Interaction between the current collector and the fluidized bed is critical, so low bed volume like 5%$V_{EC\ bed}/V_{reactor}$ showed a low current density related to the limited electron transfer from bed to the current collector. As expected, current density vastly increased once the bed volume was increased to 10%$V_{EC\ bed}/V_{reactor}$ (Fig. 3). That correlation was expected due to the higher available anode surface, where electroactive bacteria were likely to colonize the electroconductive particles, increasing the COD consumption and the electron transfer between bacteria and the electroconductive bed. Interestingly, the enhancement in COD removal and current density did not follow a linear trend over 10% $V_{EC\ bed}/V_{reactor}$ (Fig. 3), and it seemed to reach a plateau at such value, suggesting that electrode size is not limiting the microbial oxidation of pollutants. Indeed, higher installed electroconductive bed volumes (20% and 30%$V_{EC\ bed}/V_{reactor}$) led to operational problems as a rapid fluidization decline and critical clogging effects. Both undesirable phenomena reduced the electroconductive bed expansion and increased the internal resistance.

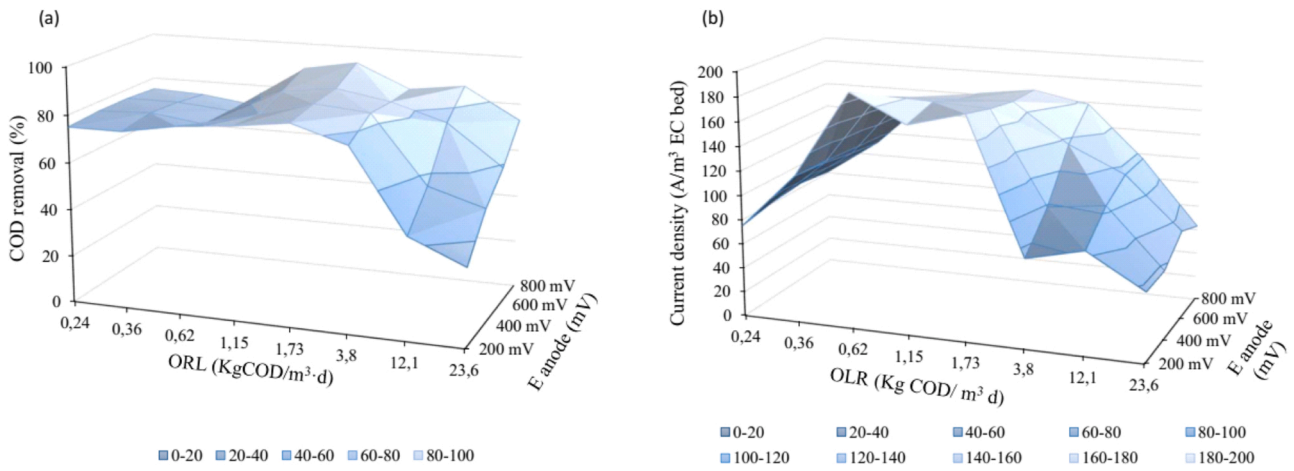

Fig. 2. **(a)** COD removal output as a function of the organic matter loading rate (OLR) and fluidized anode potential, **(b)** Current density.

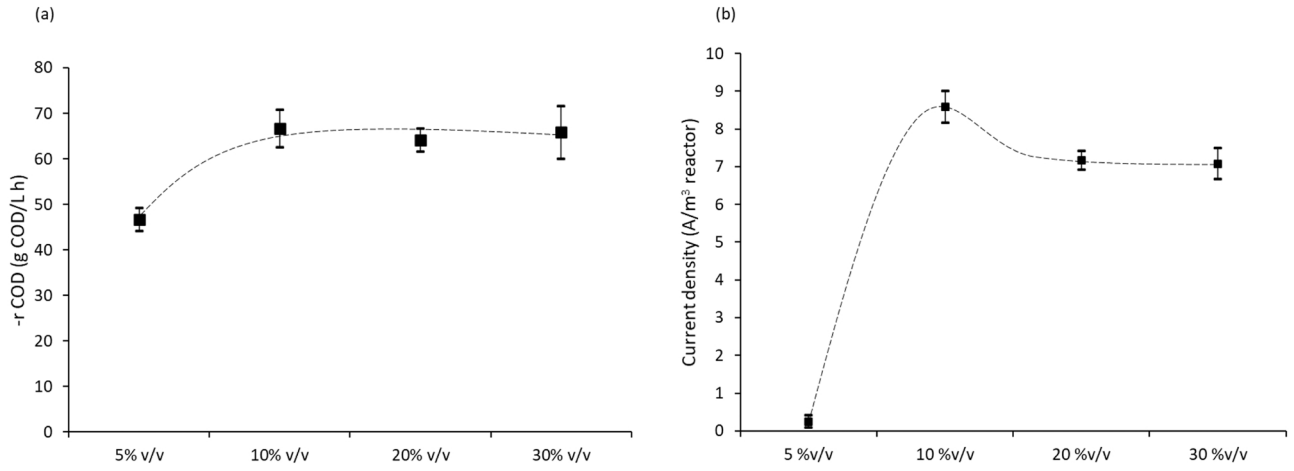

Fig. 3. Influence of the electroconductive (EC) bed volume on the wastewater treatment capacity and ME-FBR performance; **(a)** COD removal rate when operating the fluidized bed reactor at + 400 mV (V vs. Ag/AgCl), **(b)** Monitored current density at each EC scenario.

3.3. ME-FBR and energy consumption

The power consumption associated with the operation performance was also evaluated in kWh per kg of removed COD (Fig. 4). The study of this parameter is mandatory, attending to the relatively high costs related to conventional electrochemical technologies that should be overcome to the future commercialization of the ME-FBR technology. During this assay, the energy consumption was calculated just based on potentiostat consumption.

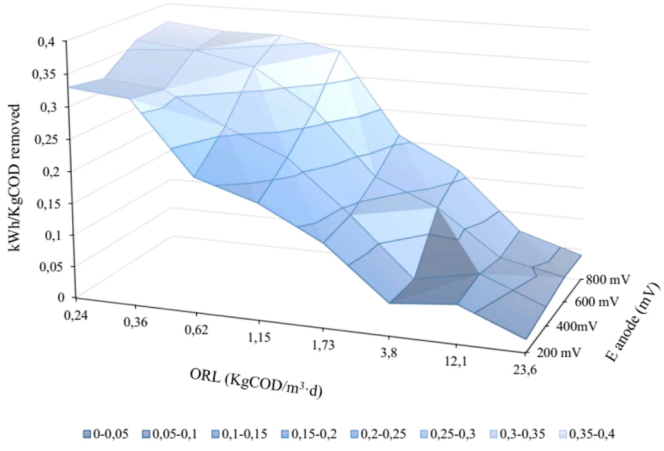

Fig. 4. Energy consumption per organic matter removed for the OLR and anode potentials tested.

The energy consumption related to this lab-scale ME-FBR revealed that the microbial technology always demanded less than 0.4 kWh kg-COD $_{\text{removed}}^{-1}$ (Fig. 4), reaching values even 10-fold lower than the required energy for aerating biological reactor in activated sludge treatments [66,67].

The final energy consumption related to ME-FBR was continuously monitored, achieving very high COD removals by only varying the applied anode potential. Furthermore, the low energy consumption was closely related to the absence of aerobic microorganisms (so oxygen supply was unnecessary), and the reduction in sludge production (no further waste management is required due to planktonic growth was not observed during operation). This fact demonstrates the validation of the technology from an operational and economic point of view.

3.4. Cathode design enhances electrical current production in ME-FBR

The potentiostat anode control is necessary to enhance the electron transport and, consequently, the pollutant removal rate. However, cathodic reactions in METs are still considered the limiting factor in many oxidative applications. During the last decades, platinum-based cathode material (Pt) was reported to reduce the cathode

overpotential by lowering the activation energy in n hydrogen production. Nevertheless, due to the high price of Pt (43 000 € kg^{-1}), it seems mandatory to evaluate other cathode materials [52]. In order to optimize the ME-FBR design, we have explored two different stainless steel cathodes with different nature to study the cathodic overpotential operating the ME-FBR with an OLR of 1.73 kgCOD m^{-3} d^{-1}: a SS mesh electrode and a SS sponge electrode. During the cathode evaluation, the anodic fluidized-bed volume was 10% $V_{EC\ bed}/V_{reactor}$.

The ME-FBR was electrochemically characterized by measuring the potential for the anode, the cathode, and the whole cell (Fig. 5.a). Potentiostat control over the anodic electroconductive material was maintained in both ME-FBR by applying an anode potential of + 400 mV (vs. Ag/AgCl, 3 M reference electrode) for a seven-days assay. The great relevance of the cathode nature evaluation was revealed by the differences between cathode potentials for mesh SS (−1.311 V) and SS sponge (−0.950 V). Attending to this, the cathodic overpotential was reduced by increasing the cathode surface area. Furthermore, the high overpotential related to the SS mesh negatively affected the energy consumption of the wastewater treatment attending to the obtained cell potentials in the mesh SS case (+1.711 V), and SS sponge one (+ 1.350 V). Furthermore, the current density decreased by ca. 20% (Fig. 5. b). Cell potentials and current density were directly related to the power consumed by the technology, so the development of low-cost materials with low cathode overpotentials (e.g. SS sponge) is required to increase the sustainability while scaling ME-FBRs.

3.5. *ME-FBR stimulates the bioelectrochemical removal of nutrients from real industrial wastewater*

The high concentration of nutrients in food and beverage industrial wastewater, as the brewery ones, is one of the main problems in the management of the corresponding industrial WWTP. The final effluent must accomplish with the national and European Directives, which are becoming more and more restrictive. Because of this, the bioelectrochemical removal of nutrients, nitrogen, and phosphorous have been evaluated in the ME-FBR at different electroconductive bed volumes (Fig. 5).

Interestingly, the electroconductive fluidized bed from ME-FBR played a key role in nutrient removal through bioelectrochemical pathways. Such bio electrochemically-assisted removal was confirmed (Fig. 6) by shifting the bed volume from 5%$V_{EC\ bed}/V_{reactor}$ to 10% $V_{EC\ bed}/V_{reactor}$, which enhanced total nitrogen (75.6 mg TN l^{-1} d^{-1}) and total phosphorous (25.8 mg TP l^{-1} d^{-1}) removal. The ME-FBR operated with 10% $V_{EC\ bed}/V_{reactor}$ enhanced the available working electrode surface, promoting electron transfer between nitrifying microbial communities and denitrifying ones leading to nitrate reduction. Our results revealed how relevant is the active surface area in this kind of fluid-like electrode, regarding the main microbial electrochemical reactions [54]. This result suggested that microbial communities growing in ME-FBR are supporting ammonium oxidation despite the anoxic conditions and the COD:N:P ratio. In addition, the high nitrate removal could be also performed in a planktonic scenario using the residual organic compounds as electron donors. It is important to point out that traditional wastewater treatment depends on the COD: N:P ratio to fully treat the raw wastewater. In addition, those conventional treatments are normally based on the transformation of pollutants into planktonic bacterial biomass (sludge) requiring a certain amount of nitrogen for protein synthesis. In contrast, ME-FBR are based on stimulating the biological oxidation of pollutants by applying an external electrode potential (polarization). This applied polarization favors the nitrogen removal minimizing the biomass production and promoting the nitrification/denitrification reactions being the ME-FBR operation less dependent on the conventional limiting COD: N:P ratio in old-fashioned treatments. This electrode-assisted microbial ammonium oxidation has been previously observed and named under the so-called electro-annamox term [68,69]. Indeed, we are currently studying the microbial community from our ME-FBR to confirm this possibility. However, when electroconductive bed volume was as large as 20% $V_{EC\ bed}/V_{reactor}$ nutrient removal was not so efficient.

4. Conclusions

This study demonstrates the high versatility of the ME-FBR technology based on the interaction between electroconductive fluidized electrodes and electroactive bacteria treating real brewery wastewaters. This situation allows a change in the paradigm of using just biofilm-based for MET applications, and suggest a new scenario where electroactive planktonic can still exhibit electrochemical behavior. Our ME-FBR was successfully validated for treating high and low strength real wastewaters, resulting in a promising technical solution regardless the ORL. The concept of polarizing a fluidized electrode as electron acceptor for bacteria resulted in lower energy consumption than supplying oxygen as happen in conventional WWTP like activated sludge or membrane bioreactors. The capacity for removing nitrogen under anoxic conditions makes ME-FBR an attractive tool to avoid costly aerobic steps for oxidizing ammonium. Furthermore, the electroconductive material

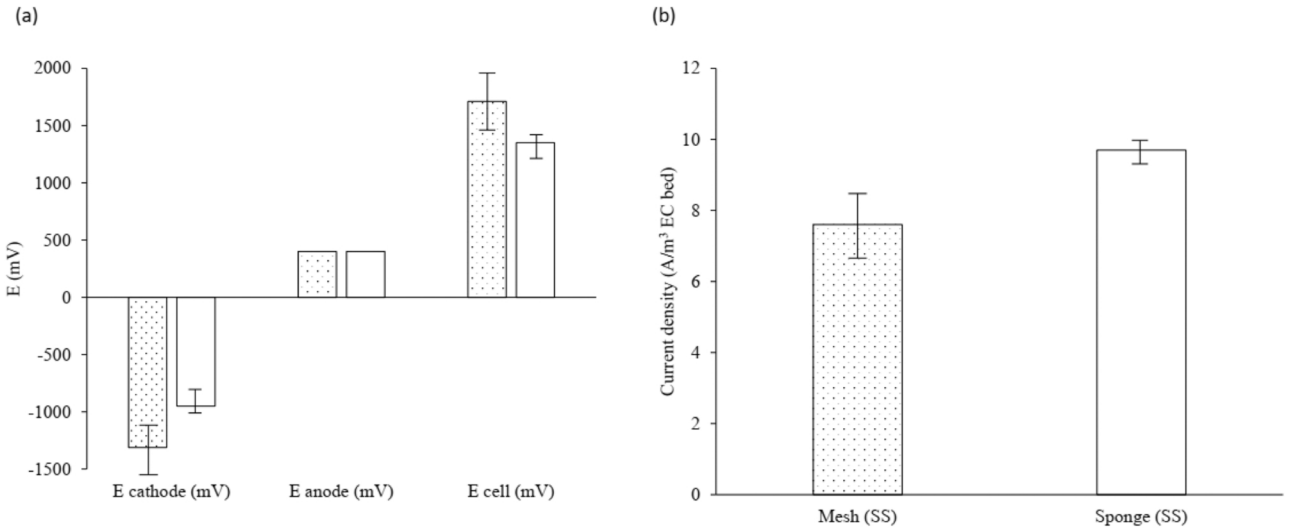

Fig. 5. Electrochemical measurements: **(a)** Cell potential and cathode potential for two cathode designs when operating the fluidized bed reactor at + 400 mV (vs Ag/AgCl), **(b)** Current output for both cathodic scenarios tested.

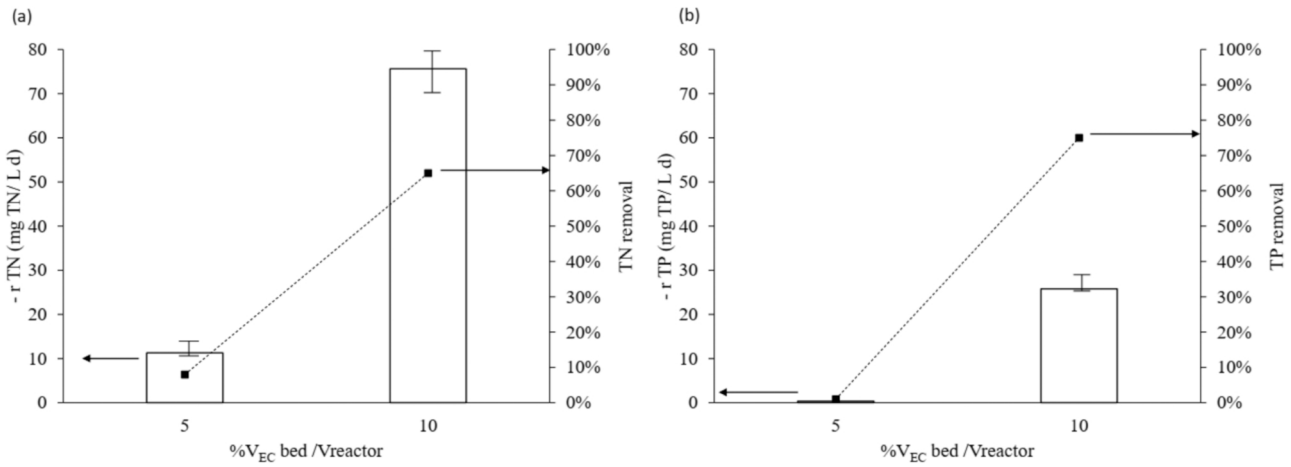

Fig. 6. Influence of the electroconductive (EC) bed volume on nutrient removal at + 400 mV (V vs. Ag/AgCl). (a) Total nitrogen removal rate and total nitrogen removal, (b) Total phosphorous removal rate and total phosphorous removal. Symbols: removal rates (bars), ■ % removal.

exhibited certain capacity for removing total phosphorus from effluent demonstrating that not just COD but also nutrients (TN and TP) was optimized to satisfy biodegradation and energy requirements. The overall optimization of the ME-FBR described in this manuscript provides a new approach for the sustainable treatment of brewery wastewaters, that we believe can be applied to additional industrial pollutants.

CRediT author Statement contributions

YA carried out most of the experiments and drafted the manuscript. VM designed the study. MLL, ST-S, PF-L helped with the experimental work. JMO, JFC, FR, and AE-N supervised the study and corrected the manuscript. All authors read and approved the final manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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