



Merging microbial electrochemical systems with electrocoagulation pretreatment for achieving a complete treatment of brewery wastewater



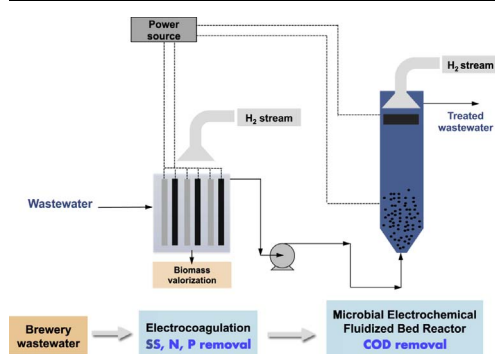
Sara Tejedor-Sanz^{a,b}, Juan Manuel Ortiz^{b,c}, Abraham Esteve-Núñez^{a,b,*}

^a University of Alcalá, Department of Chemical Engineering, Ctra. Madrid-Barcelona, km. 33,6, 28871, Alcalá de Henares, Madrid, Spain

^b IMDEA Water Institute, Av. Punto Com, 2, 28805 Alcalá de Henares, Madrid, Spain

^c CC Aqualia, Department of Innovation and Technology, Av. Camino de Santiago 40, 28050 Madrid, Spain

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Electrocoagulation
Microbial electrochemical technologies (METs)
Fluidized anode
Combined wastewater technologies
Brewery wastewater

ABSTRACT

The limitations of microbial electrochemical technologies (METs) for full-scale wastewater treatment suggest the need for supporting these systems with a complementary technology. In this study we propose the integration of two electrochemical techniques to fully treat brewery effluents: an electrocoagulation (EC) and a microbial electrochemical fluidized bed reactor (ME-FBR). The EC pretreatment effectively removed most of the suspended matter and the nutrients of the effluent. We investigated the influence of current density and the reaction time on the EC performance. Varying these parameters allowed to fine-tune the removal of nutrients in this first treatment stage, obtaining removals from 30 to 98% of nitrogen and from 25 to 99% of phosphorus. The effluent of the EC was continuously fed into a ME-FBR (organic loading rate of $1.15 \text{ kg-COD m}^{-3}\text{d}^{-1}$) with a fluidized and polarized anode (0.2 V vs Ag/AgCl) colonized with electroactive biofilm. This second step oxidized the soluble organic matter using a fluidized anode as terminal electron acceptor and harvesting current density values of 25 A m^{-3} . With this novel technological tandem, it was possible to remove a 93% of nitrogen, 98% of phosphorus, 93% of the total suspended solids, and > 88% of the COD of a brewery wastewater.

1. Introduction

Microbial electrochemical technologies represent a promising field based on the effective redox coupling between microbial metabolism

and electrically conductive materials [1]. Regarding the environmental applications of METs, in the wastewater treatment field these novel systems can potentially represent an alternative to classical technologies. In a microbial electrochemical wastewater treatment, a

* Corresponding author at: Bioelectrogenesis Group, Chemical Engineering Department, University of Alcalá, Madrid, Spain.

E-mail addresses: sara.tejedor@imdea.org (S. Tejedor-Sanz), juanma.ortiz@imdea.org (J.M. Ortiz), abraham.esteve@uah.es (A. Esteve-Núñez).

<http://dx.doi.org/10.1016/j.cej.2017.08.049>

Received 13 June 2017; Received in revised form 8 August 2017; Accepted 11 August 2017

Available online 12 August 2017

1385-8947/ © 2017 Published by Elsevier B.V.

community of electroactive microorganisms catalyze the oxidation of organic matter donating the resulting electrons to an anode generating an electric current [2,3]. These electrons are then transferred to a cathode for harvesting electricity in a microbial fuel cell (MFC), or to a counter electrode under potentiostatic control in a microbial electrolysis cell (MEC). The main bottlenecks for scaling-up METs are the problems related to using static biofilm-based electrodes: the mass transfer limitation between solution and active microorganisms, the low active surface area of the electrode and the pH drop along the electroactive biofilm [4]. To deal with this problem, METs can benefit from a novel concept where the classical static electrode is replaced by a fluid-like electrode made of carbon microparticles as part of a microbial electrochemical-fluidized bed reactor (ME-FBR) [5]. In this configuration the anode maintains a fluid-like state and serves as electron acceptor for electroactive microorganisms. The ME-FBR design presents some advantages over other microbial electrochemical configurations. It hosts features of classical anaerobic fluidized bed reactors: e.g. a carrier for biomass growth so cells wash-out can be minimized, high mass and temperature transport together with proper mixing inside the reactor [6]. Moreover, this configuration includes a 3D electrode that confers high surface area to electroactive microorganisms. Different approaches of electrodes in motion, either constructed of stirred conductive granules [7] or made of capacitive conductive granules [8], which recirculate through an external discharge cell, have been reported to accept electrons from mixed populations. Many METs require complex designs, with expensive components such as a membrane for separating anode and cathode chambers thus complicating the possibility of up-scaling the configuration. The ME-FBR is a single chamber reactor, relatively easy to operate. Other designs are modulated systems that can enhance treatment capacity by operating several modulated units in parallel or serial [9]. However, for treating large volumes of wastewater at full-scale, these kind of configurations may not be economically viable.

Although urban wastewater [10,11] has been the most common biodegradable fuel tested in METs, industrial organic matter sources have been extensively tested in the last decade [12–14]. Food industry effluents have gained much attention since their organic matters are easily oxidized by microorganisms and thus are considered as ideal fuels for METs. From the very beginning, the treatment of brewery wastewater with METs has received much attention [15,16]. In this wastewater the organic matter is typically treated by aerobic methods or by anaerobic digestion in UASB or fluidized bed reactors, whereas nutrients (N and P) are eliminated in aeration tanks or by physico-chemical processes [17]. Brewery wastewater treatment has been successfully treated in a 90 L stackable baffled MFC with a net energy generation of $21\text{--}34\text{ W m}^{-3}$ and organic matter removal up to of 88% [15]. Zuang et al. (2011) designed a 10-liter serpentine-type MFC for the treatment of brewery effluent as well, achieving power outputs of 4.1 W m^{-3} (0.7 A m^{-3}), COD removals of $0.9\text{ kg COD d}^{-1}\text{ m}^{-3}$ and coulombic efficiencies (CE) (fraction of electrogenic organic matter degradation) of 8% [18]. Nutrients removal in bioelectrochemical systems is one of the main challenges that the field faces. METs cannot completely perform the treatment of a wastewater by themselves and it becomes necessary the complementation of them with other technologies. Currently, there are no reports describing scalable prototypes able to deal with both nitrogen and phosphorus removal. Although some studies have reported simultaneous organic matter and nutrients removal from wastewaters in microbial electrolysis cells or microbial fuel cells [19–21], the most effective strategy for optimizing the treatment of these pollutants might be the separation of the two processes. Specifically, the degradation of organic matter in brewery effluents in bioelectrochemical systems has been extensively studied, however, none of these studies have proposed a method for removing the nutrients of this wastewater [15,16,22].

For the scaling-up process, continuous flow (low residence time values and large water volumes treatment), single-compartment METs

and membrane-less are favored for wastewater treatment. Wastewater infrastructure is expensive to build and typically is designed to last at about 50 years. One of the challenges on the reactor design is be able to exploit the existing built structures of wastewater treatment plants (like the fluidized configurations). This would eliminate a great part of the initial investments costs associated to the implementation of a bioelectrochemical wastewater treatment. The development of hybrid MET-based systems, as METlands (wetland plus a MET) [23] or membrane bioreactor MFCs [24], is currently gaining much attention in the field [25]. Merging several technologies allows incorporating the respective merits of each individual technology into the same treatment. For instance, recently Feng et al. combined two kind of electrochemical-based technologies, a microbial fuel cell, and a capacitive deionization cell, for removing the organic matter (90% of COD) and the soluble nutrients (63% of total nitrogen and 30% of phosphates), respectively [26].

In this context, electrocoagulation, which has been widely used to remove the suspended matter and nutrients from industrial effluents [27–29], could complement METs to achieve a full wastewater treatment. Several studies have already proposed hybrid systems based on the integration of electrocoagulation with other technologies such as biological reactors [30–33].

Thus, we propose for the first time the integration of electrocoagulation with a bioelectrochemical-based system for treating a brewery wastewater as a suitable strategy for completely treating a brewery wastewater. First, an electrocoagulation (EC) step where suspended solids and bound nutrients are removed. Second, we have merged a classical fluidized reactor with MET resulting in a ME-FBR for treating the organic matter. This study constitutes a proof of concept of the combination of two treatment systems and that could be extrapolated to other kind of industry effluents.

2. Materials and methods

2.1. Wastewater description and analysis

All wastewater samples used for the experiments were collected on the same day from the brewery plant Mahou-San Miguel in Alovera, Guadalajara, and stored at $4\text{ }^{\circ}\text{C}$ until used. Wastewater samples were taken from the homogenization tank that harvests different effluents of the brewery production line.

2.2. Analytical methods

Wastewater samples were analyzed according to the Standard Methods for the Examination of Water and Wastewater [34]. Samples were frozen at $-20\text{ }^{\circ}\text{C}$ prior to their analysis. COD, total N and total P were measured with a commercial kit in a Spectroquant TR420 and a Spectroquant Pharo 100 from Merck. Total organic carbon (TOC) analyses were performed in an Organic Carbon Analyzer TOC-V CSH from Shimadzu. Total suspended solids (TSS) were determined by vacuum filtration using AP40 90 mm filters from Millipore. The conductivity was measured with a conductimeter MM41 and the pH with a pHmeter 25 (Crison). The turbidity was determined with a TubiDirect (Lovibond), and the color with a PCcheckit (Lovibond). Alkalinity tests were performed by titration system model 809 from Metrohm. Ammonium and nitrate were measured in a Metrohm Advanced Compact IC model 861 with two channels.

2.3. Electrocoagulation procedure

The electrocoagulation cell consisted of a cylindrical vessel with a capacity of 2 L, in which four electrodes, two of aluminum and two graphite plates, were immersed. The electrode size was $13 \times 9\text{ cm}$, the thickness of the aluminum plates was 0.1 cm, while for graphite plates was 0.2 cm. At the top, each electrode had a small rectangular contact used to connect wires. The separation between electrodes was 1 cm,

with each aluminum electrode facing a graphite electrode. They were attached to two nylon rods at their uppermost parts. EC experiments were performed using a power supply Elektro-Automatik PS 2016–100 (0→16 V, 0→10 A) and a Fluke 177 True RMS multimeter was used for measuring the current and voltage applied. The EC cell was constantly stirred at 900 rpm. All experiments were performed at room temperature (23–28 °C). Two sets of experiments were performed in the EC. First, the reaction time (RT) of the wastewater in the cell was maintained constant (15 min) and the current density (j) was varied (2.6, 5 and 10 mA cm⁻²). Second, j was fixed to 5.0 mA cm⁻² and the RT was changed (5, 10 and 15 min). The last step of the process was filtration using filter paper. Raw wastewater was renewed in the cell for each test. The treatment capacity (TC) for each assay was calculated by dividing the volume of wastewater treated (2 L) by the RT and the electrodes area.

2.4. Microbial electrochemical-fluidized bed reactor (ME-FBR)

The ME-FBR consisted of a glass column (4.6 cm of internal diameter (ID) and 30 cm height) with a conical bottom (4.6 cm in ID and 5.2 cm height). The top of the ME-FBR was sealed for maintaining an anoxic environment. For fluidizing, a recirculation flow was drawn from the top section using a peristaltic pump, Heidolph 5006. The medium was fed downwards with an elbow that drove the flow to the vertex of the conical bottom, resulting in a rising flow of fluid through the column. The electrolyte velocity used during all the experimental periods was of 0.46 cm s⁻¹. The total working volume of the reactor was 0.68 L (including the recirculation tube and the bed volume). The anode consisted of a bed composed of 80 mL of activated carbon particles (0.6–1 mm diameter, Aquacarb, Chemviron). A graphite plate (2 × 8 cm) vertically immersed in the fluidized bed was used as current collector. The cathode was made of a 10 × 7 × 0.6 cm piece graphite felt (RGV 2000, Mersen). An Ag/AgCl 3 M KCl electrode (HANNA) was employed as a reference electrode. The ME-FBR was operated as a three-electrode electrochemical cell and the fluidized bed worked as the anode by polarizing it to 0.2 V (all potentials are reported versus Ag/AgCl electrode). The potentiostat used was a NEV3 Nanoelectra. The reactor was inoculated with sludge from a wastewater treatment plant and was previously operated during 5 months first at batch mode and second, at continuous mode, with brewery wastewater as influent without EC pretreatment. A peristaltic pump (Watson and Marlow, 205S) was used for continuously feeding the reactor with wastewater from an inlet port placed at the bottom of the column. The effluent port was located at upper part of the reactor. The hydraulic retention time in the ME-FBR was of 2.4 days. Samples were collected dairy and kept at -20 °C for subsequent analysis. The current density values for the ME-FBR are given as current per net reactor volume (NRV) (0.6 L).

3. Results and discussion

The analytical results from the brewery wastewater characterization (Table 1) showed a complex effluent with a high content of TSS and COD. Ammonium and nitrate were below the detection limits, indicating that all the nitrogen in the wastewater was in the form of suspended and complex matter. Furthermore, phosphorus concentration in the raw wastewater was relatively high (15.2 ppm). We proceed to treat the effluent through two sequential stages: first, in a EC cell and, second, in a ME-FBR. Fig. 1 shows a diagram of the combined process used with the possibility of recovering added-value by-products from the treatment.

3.1. Electrocoagulation for removing solids and nutrients

Electrocoagulation is an electrochemical technique closely related to chemical coagulation. It involves supplying coagulant ions (Al³⁺, Fe³⁺) by the application of an electric current to a sacrificial anode

Table 1

Chemical and physical parameters of the brewery wastewater and the effluents after both EC and ME-FBR treatments.

Parameter	Brewery WW	Effluent from EC	Effluent from ME-FBR
STOC (mg L ⁻¹)	887 ± 60	843 ± 15	122 ± 32
COD (mg L ⁻¹)	2888 ± 153	2757 ± 84	356 ± 43
NO ₃ ⁻ (mg L ⁻¹)	n.d	4.3 ± 0.9	0.9 ± 1
NH ₄ ⁺ (mg L ⁻¹)	n.d	7.3 ± 1	n.d
Total N (mg L ⁻¹)	66.3 ± 5.5	9.3 ± 1.6	< 5
SO ₄ ⁻ (mg L ⁻¹)	21.8	12.4 ± 1	4.6 ± 1
Total P (mg L ⁻¹)	15.1 ± 1	0.6 ± 0.1	0.3 ± 0.2
TSS (mg L ⁻¹)	625 ± 23	70 ± 23	47 ± 17
Alkalinity (ppm CaCO ₃)	1163	1087	1330
pH	7	8.2	9.1
Conductivity (mS cm ⁻²)	2.8	2.58	2.50
Turbidity (UNT)	447	29	6.3
Color (mg L ⁻¹ Pt-Co)	4180	315	110

placed into a processing tank [35]. In our EC, aluminum was provided as electrochemical coagulant coming from the oxidation of aluminum plates acting as sacrificial anodes. When our raw brewery wastewater was treated by EC, the removal of the colloidal matter in it was significant in all tests performed. Fig. 2A shows the experiments for constant current density at different treatment capacities. As it is observed, for the lowest treatment capacity of our EC cell, 0.17 m³ m⁻² h⁻¹ (RT = 15 min), a 96% and 98% of the P and N, respectively, was removed from the wastewater. Meanwhile, the COD content decreased by 20% and the TSS by 89%. The performance was significantly affected by the variation of the treatment capacity of the cell. By decreasing this parameter, the operating time of the EC cell with the wastewater was enhanced. Thus, a larger amount of coagulant was electrogenerated and, as a result, a larger amount of suspended particles were destabilized. However, the decrease in the removal of nutrients and COD did not show a proportional relation with the treatment capacity. For example, operating the EC cell with a 3-fold increased treatment capacity (from 0.17 m³ m⁻² h⁻¹ to 0.51 m³ m⁻² h⁻¹) did not produce a proportional reduction on the removal of COD, TSS, N and P. Additionally, when the treatment capacity in the cell was reduced by half (from 0.51 m³ m⁻² h⁻¹ to 0.26 m³ m⁻² h⁻¹) the removal of P and N, clearly marked, and of the COD, was higher than 2-fold. These effects could be related to the time needed for the aggregates and flocks to be formed in the bulk medium.

The results for the series of assays where current density was the variable term and the treatment capacity remained constant are shown in Fig. 2B. By applying higher current densities in the EC cell, the coagulant (i.e. Al(OH)₃) was electrochemically generated at higher rates. This could either increase the treatment capacity of the reactor or decrease the required reactor size. In our EC unit, increasing j from 2.6 to 5 mA cm⁻² did not show any difference in the removal of P whereas the removal of N, COD, and TSS showed a slight enhancement, suggesting that both could be further eliminated by electrogenerating more coagulant. Actually, the COD and TSS removal had the same proportional increase in all the assays with a fixed treatment capacity. We hypothesize that the nature of the colloidal matter could be mainly organic. Increasing further the current to 10 mA cm⁻² did not significantly affect the removal rate of nutrients and COD, indicating that all the particulate matter capable of being destabilized had been at 5 mA cm⁻². Regarding COD removal, we can assume that under non-limiting coagulant (i.e. Al(OH)₃) conditions, the remaining COD was due to the soluble fraction contained in the wastewater. Specifically, COD could not be removed further than 21%, a result that matches well with the COD solubility of the brewery wastewater. It is remarkable that an optimal EC performance was able to reach levels of nutrients as low as 0.2 mg L⁻¹ of P and 1.2 mg L⁻¹ of N. These residual concentrations could be further tuned by varying either the current density

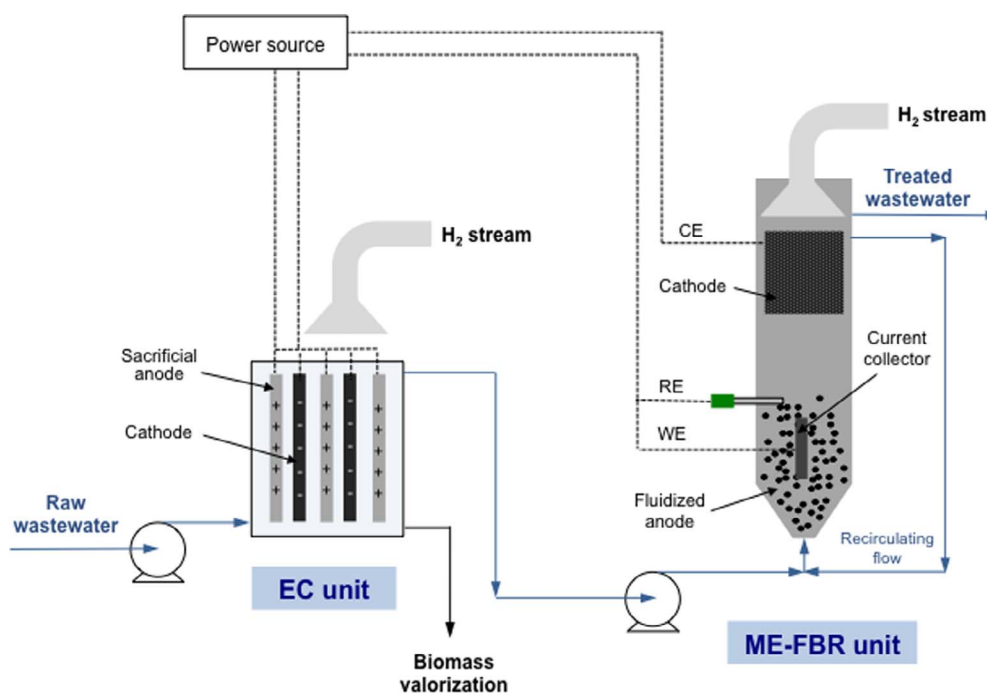


Fig. 1. Schematic of the process proposed for the treatment of a brewery wastewater as a sustainable methodology with added-value by-products (hydrogen and the biomass from the EC).

or the treatment capacity of the EC.

Our results revealed that the nutrients removed by the EC treatment were mainly associated to the particulate matter present in the brewery effluent. Although the EC removed a majority of the nutrients, residual concentrations were enough to fulfill the metabolic requirements for the catabolic reactions in the following biological reactor for the experimental period (12 days). In the raw brewery effluent, the initial ratio COD:N:P was of approximately 500:11:3, and after the EC treatment, this ratio was decreased to values as low as 500:0.4:0.1. This ratio is below the nutrients requirements reported for the biomass growth in anaerobic digesters [36]. However, it was enough for satisfying the anabolic demand of the microbial community in our ME-FBR during the whole experimental period.

The power, aluminum consumption and the cost of the EC treatment for the different conditions tested in the EC are shown in the Supplementary Table 1. Regarding the power consumption, the energy requirements for the EC reactor have been reported to be easily powered by a renewable energy [29].

Finally, optimal operation conditions of the EC, in terms of removal

performance with minimum energy consumption, were established ($j = 5 \text{ mA cm}^{-2}$, treatment capacity of $0.17 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$) to generate an effluent ready to be treated in the following step: the ME-FBR.

3.2. Microbial electrochemical-fluidized bed reactor for removing soluble COD

The effluent from the EC (the influent in the second stage) had a low content of particulate organic matter since the majority of the colloidal organic fraction had been removed in the EC (TSS of 70 mg L^{-1} , Table 1). Therefore, the COD in the influent of the ME-FBR had mostly soluble matter as minor fermentation compounds (sugars), soluble protein matter and organic acids. Thus, fermentation processes, conversions of complex organics into volatile fatty acids (VFAs) by acidogens, acetogenesis, microbial electrogenesis (current harvesting), and methanogenesis were simultaneously occurring in the ME-FBR. The microbial community of this reactor was already adapted to treating a brewery effluent as it was previously exposed to it. However, it was the first time that this bioreactor was fed with an effluent coming from an

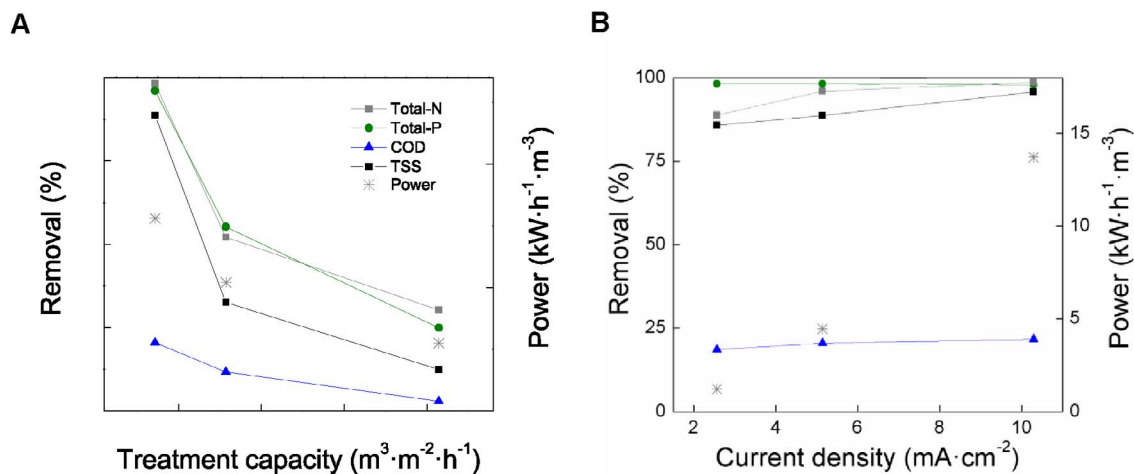


Fig. 2. Removal of COD, TSS and nutrients, and power consumption of the EC cell at the different tests. A) At different treatment capacities and at a fixed current density of 5 mA cm^{-2} . B) At different current densities and at a constant treatment capacity of $0.17 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ (RT = 15 min).

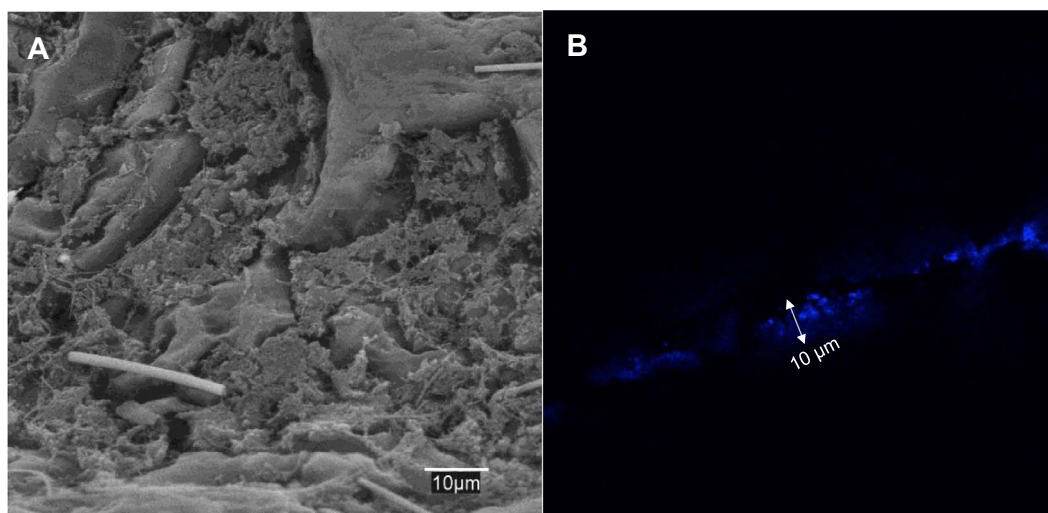


Fig. 3. A. Microbial colonization of the fluidized anodic particles of the ME-FBR. B. Biofilm thickness taken with confocal microscopy using DAPI as stain.

electrocoagulation treatment. At this point, the fluidized particles were colonized with a biofilm of *ca.* 10 µm of thickness (Fig. 3A and B). The colonization was heterogeneous and the biomass was concentrated at the big pores of the particles as can be observed in Fig. 3A.

The EC effluent was fed at an organic loading rate of 1.15 kg-COD $m^{-3} d^{-1}$ into the ME-FBR (HRT of 2.4 days) and efficiently removed 87% of the total COD. Moreover, more than 50% of the TSS that remained in the wastewater after the electrocoagulation step was further removed, reducing the turbidity and color of the effluent. Nitrogen and phosphorus were removed as well throughout this second step, remaining in the final effluent at trace levels (Fig. 4 and Table 1). We attribute this minor reduction to the use of these nutrients by microorganisms for biomass synthesis. Interestingly, sulphate was reduced in the ME-FBR by 63%, revealing the presence of sulphate reducing bacteria (SRB). These bacteria compete with electrogens for VFAs and even for other sources of electrons in the wastewater such as ethanol, aromatic compounds or the hydrogen produced either at the cathode or by acetogenic bacteria [37]. However, if we estimate the theoretical COD required to reduce all the sulphate in the wastewater, it accounts for less than 1% of the organic matter available in the influent fed into the ME-FBR. The operation of this reactor produced an alkalization of the

effluent that eventually reached a pH of 9. This pH increase could be due to a local increase of the alkaline content at the vicinity of the cathode, where the effluent outlet is located. The consumption of VFAs in the medium could also be responsible for the alkalization of the effluent.

Electrical current was harvested just after inoculation indicating that the electroactive bacteria were already adapted to degrade the organic matter transferring the resulting electrons to the fluidized anode (Fig. 5). This result confirmed us that EC pretreatment did not inhibit the bioelectrochemical degradation of the brewery wastewater. The current harvested reached a stationary value from the 4th day of operation of 25 A m_{NRV}^{-3} (214 A $m^{-3} bed$). Regarding the cathode potential, it remained between -0.95 and -1.05 V during the experimental period. In the absence of oxygen inside the ME-FBR, at those potentials water is likely to be reduced to form hydrogen at this electrode. The average coulombic efficiency was of 17%, calculated over the total COD removed in the ME-FBR. As it is expected during the treatment of a real wastewater, this CE value is low as compared to those ones obtained with acetate-fed bioelectrochemical systems [5]. This can be due to several factors. Firstly, not all the electrons stored in the organic matter are available for the electroactive microorganisms; for instance, the acidogens can perform beta-oxidative reactions of long chain fatty acids, which have not been previously reported as suitable electron donors for electrogens. Secondly, electroactive bacteria compete with acetogenic bacteria and methanogens for the electrons at the

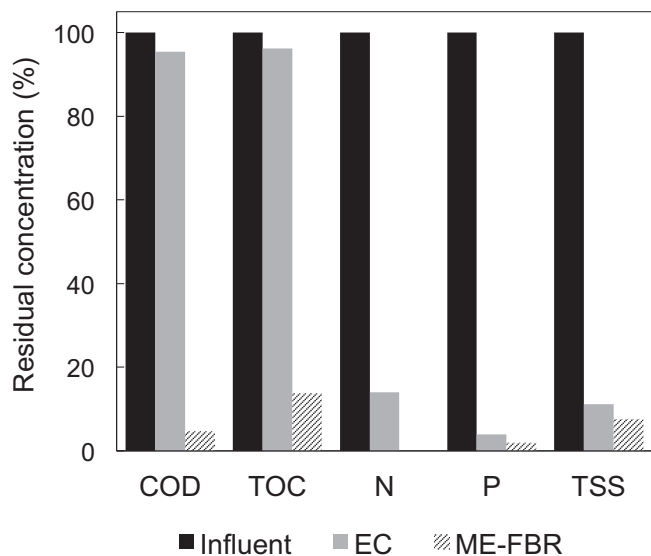


Fig. 4. Residual concentration (as a percentage) of COD, TOC, N, P and TSS in the wastewater after the different treatments.

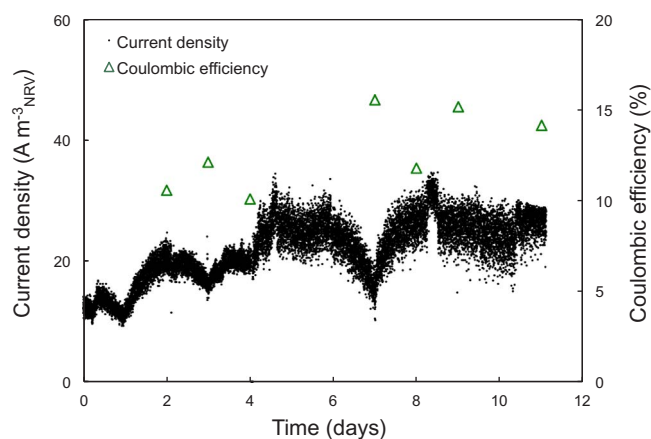


Fig. 5. Current density production and coulombic efficiency during the operation at continuous mode of the ME-FBR.

very last steps of the organic matter oxidation. Future research focused on studying the effects of varying the anode potential, bed expansion, the HTR or the pH could optimize the performance of this reactor in terms of COD removal and current harvesting. Regarding the energy consumption, the ME-FBR consumed an average of 1.8 kWh (kg-COD removed)⁻¹.

3.3. EC + ME-FBR process for treating brewery wastewater

Overall, the whole process EC+ME-FBR could remove a 93% of nitrogen, 98% of phosphorus, 93% of the total suspended solids, and > 88% of the COD of a brewery wastewater (Table 1). The limiting step of this strategy shown here as a proof of concept is the ME-FBR, which operates at higher retention times than the electrocoagulation cell. Trace levels of total nitrogen (< 5 mg L⁻¹) and phosphorous (0.3 mg L⁻¹) in the effluent could be achieved throughout the global process as a result of the electrocoagulation stage and assimilation reactions by the microbial community at the ME-FBR. Special attention should be paid to the COD removed at the biological step in order to not exceed the discharge limits. Varying the ME-FBR operating parameters such as the HRT or anode potential could allow controlling the organic matter degradation rate in this configuration.

Brewery wastewater has been treated through a large variety of process. Anaerobic digesters, membrane bioreactors or combined anaerobic/aerobic bioreactor allow achieving COD removals over 90% operating at higher organic loads than our ME-FBR [17]. Compared to other wastewater treatment systems based on the integration of two different electrochemical-based technologies including a biological step, like a capacitive deionization cell, our strategy results to be more efficient on the removal of nutrients [26]. In addition, our electrocoagulation pretreatment for removing the suspended matter was able to reach values of nutrients in the effluent as low as 0.2 mg L⁻¹ for total phosphorous and 1.2 mg L⁻¹ for total nitrogen, which have not been achieved with other combined systems such as the ones using a biological reactor with Fenton and coagulation processes [38]. Electrocoagulation has already been proposed in combination with biological reactors such as a rotating and a membrane bioreactor [32]. However, in that study the EC was set as a post-treatment for removing phosphorous of a municipal wastewater, which presented an organic load much lower than our brewery wastewater and therefore the operating conditions for the EC were milder. Other studies have used as well EC as a post-treatment in order to remove the refractory organic compounds of landfill leachate after a biological treatment [39]. Compared to those strategies in which nitrogen was biologically removed via nitrification/denitrification processes, our proposal removed higher levels of total nitrogen at the EC pretreatment. Unlike this kind of biological treatment, the nutrients removal efficiency of our integrated system does not depend on the organic matter content of the wastewater. Regarding phosphorous removal, both studies effectively removed it at the electrocoagulation step, achieving trace levels the effluent, as did the EC + ME-FBR tandem.

One of the potential points of the EC + ME-FBR strategy for treating industrial effluents is the chance to recover the hydrogen generated at the cathodes of the electrochemical processes. Additionally, the sludge produced at the EC, which is rich in nutrients and organic matter could be recycled, for instance, as fertilizer. Moreover, compacted aluminum waste produced in beverage industry could be used for sacrificial anodes in EC units.

4. Conclusions

This study demonstrates the compatibility of two technologies based on electrode-mediated reactions for effectively treating brewery wastewater. The EC pretreatment was able to remove the insoluble matter containing most of the nutrients and a fraction of the total COD. The reaction time and the current density circulating through the EC reactor

could be fine-tuned to obtain different qualities of the effluent (TSS, TN and TP). The soluble organic matter of the brewery wastewater was oxidized in a bioelectrochemical treatment (ME-FBR) with a fluidized anode serving as electron acceptor for electroactive bacteria. This tandem of electrochemical technologies can be a flexible and versatile platform for treating industrial wastewaters. The full process (EC + ME-FBR) is a perfect example of a strategy in context of the water-energy nexus. The economical and the environmental sustainability of the process rely on the use of the by-products generated at each stage and the minimization of the energy demand of the process. Overall, our proposal of merging EC with ME-FBRs provides a new approach for brewery wastewater treatment while offering a valuable alternative to energy generation and sub-product recovery.

Acknowledgments

This research was supported by the Center for the Development of Industrial Technology (CDTI, Spain), Spanish Ministry of Economy and Competitiveness, through the project ITACA (INNPRONTA program, CEN-20091005), and by the European Commission through the project ANSWER (Advanced Nutrient Solutions With Electrochemical Recovery, LIFE programme, LIFE15ENV/ES/00059).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.08.049>.

References

- [1] Z. Du, H. Li, T. Gu, A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy, *Biotechnol. Adv.* 25 (2007) 464–482.
- [2] H. Wang, Z.J. Ren, A comprehensive review of microbial electrochemical systems as a platform technology, *Biotechnol. Adv.* 31 (2013) 1796–1807.
- [3] B.E. Logan, K. Rabaey, Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies, *Science* 337 (2012) 686–690.
- [4] K. Scott, E.H. Yu, *Microbial Electrochemical and Fuel Cells: Fundamentals and Applications*, Woodhead Publishing, 2015.
- [5] S. Tejedor-Sanz, J.R. Quejigo, A. Berná, A. Esteve-Núñez, The planktonic relationship between fluid-like electrodes and bacteria: wiring in motion, *ChemSusChem* 10 (2017) 693.
- [6] J.J. Heijnen, A. Mulder, W. Enger, F. Hoeks, Review on the application of anaerobic fluidized bed reactors in waste-water treatment, *Chem. Eng. J.* 41 (1989) B37–B50.
- [7] J. Liu, F. Zhang, W. He, X. Zhang, Y. Feng, B.E. Logan, Intermittent contact of fluidized anode particles containing exoelectrogenic biofilms for continuous power generation in microbial fuel cells, *J. Power Sources* 261 (2014) 278–284.
- [8] A. Deeke, T.H.J.A. Sleutels, T.F.W. Donkers, H.V.M. Hamelers, C.J.N. Buisman, A. Ter Heijne, Fluidized capacitive bioanode as a novel reactor concept for the microbial fuel cell, *Environ. Sci. Technol.* 49 (2015) 1929–1935.
- [9] L. Zhuang, Y. Zheng, S. Zhou, Y. Yuan, H. Yuan, Y. Chen, Scalable microbial fuel cell (MFC) stack for continuous real wastewater treatment, *Bioresour. Technol.* 106 (2012) 82–88.
- [10] R.K. Brown, F. Harnisch, T. Dockhorn, U. Schröder, Examining sludge production in bioelectrochemical systems treating domestic wastewater, *Bioresour. Technol.* 198 (2015) 913–917.
- [11] B. Min, B.E. Logan, Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell, *Environ. Sci. Technol.* 38 (2004) 5809–5814.
- [12] B. Cercado-Quezada, M.-L. Delia, A. Bergel, Testing various food-industry wastes for electricity production in microbial fuel cell, *Bioresour. Technol.* 101 (2010) 2748–2754.
- [13] A.Y. Çetinkaya, E.O. Koroğlu, N.M. Demir, D.Y. Baysoy, B. Özkaya, M. Çakmakçı, Electricity production by a microbial fuel cell fueled by brewery wastewater and the factors in its membrane deterioration, *Chin. J. Catal.* 36 (2015) 1068–1076.
- [14] P.T. Kelly, Z. He, Understanding the application niche of microbial fuel cells in a cheese wastewater treatment process, *Bioresour. Technol.* 157 (2014) 154–160.
- [15] Y. Dong, Y. Qu, W. He, Y. Du, J. Liu, X. Han, Y. Feng, A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode, *Bioresour. Technol.* 195 (2015) 66–72.
- [16] Y. Feng, X. Wang, B.E. Logan, H. Lee, Brewery wastewater treatment using air-cathode microbial fuel cells, *Appl. Microbiol. Biotechnol.* 78 (2008) 873–880.
- [17] G.S. Simate, J. Cluett, S.E. Iyuke, E.T. Musapatika, S. Ndlovu, L.F. Walubita, A.E. Alvarez, The treatment of brewery wastewater for reuse: state of the art, *Desalination* 273 (2011) 235–247.
- [18] L. Zhuang, Y. Yuan, Y. Wang, S. Zhou, Long-term evaluation of a 10-liter serpentine-

- type microbial fuel cell stack treating brewery wastewater, *Bioresour. Technol.* 123 (2012) 406–412.
- [19] S. Tejedor-Sanz, T. Bacchetti, J.J. Salas, L. Pastor, A. Esteve-Núñez, Integrating a Microbial Electrochemical System in a classical wastewater treatment configuration for removing nitrogen from low COD effluents, *Environ. Sci. Water Res. Technol.* 2 (2016) 884–893.
- [20] B. Virdis, K. Rabaey, R.A. Rozendal, Z. Yuan, J. Keller, Simultaneous nitrification, denitrification and carbon removal in microbial fuel cells, *Water Res.* 44 (2010) 2970–2980.
- [21] Y. Zhang, J.S. Noori, I. Angelidaki, Simultaneous organic carbon, nutrients removal and energy production in a photomicrobial fuel cell (PFC), *Energy Environ. Sci.* 4 (2011) 4340–4346.
- [22] E.O. Koroğlu, B. Özkaya, C. Denктаş, M. Çakmakci, Electricity generating capacity and performance deterioration of a microbial fuel cell fed with beer brewery wastewater, *J. Biosci. Bioeng.* 118 (2014) 672–678.
- [23] A. Aguirre-Sierra, T.B.-D. Gregoris, A. Berná, J.J. Salas, C. Aragón, A. Esteve-Núñez, Microbial electrochemical systems outperform fixed-bed biofilters in cleaning up urban wastewater, *Environ. Sci. Water Res. Technol.* 2 (2016) 984–993.
- [24] L. Malaeb, K.P. Katuri, B.E. Logan, H. Maab, S.P. Nunes, P.E. Saikaly, A hybrid microbial fuel cell membrane bioreactor with a conductive ultrafiltration membrane biocathode for wastewater treatment, *Environ. Sci. Technol.* 47 (2013) 11821–11828.
- [25] L. Xu, Y. Zhao, L. Doherty, Y. Hu, X. Hao, The integrated processes for wastewater treatment based on the principle of microbial fuel cells: a review, *Crit. Rev. Environ. Sci. Technol.* 46 (2016) 60–91.
- [26] C. Feng, C.-C. Tsai, C.-Y. Ma, C.-P. Yu, C.-H. Hou, Integrating cost-effective microbial fuel cells and energy-efficient capacitive deionization for advanced domestic wastewater treatment, *Chem. Eng. J.* 330 (2017) 1–10.
- [27] A.S. Fajardo, R.F. Rodrigues, R.C. Martins, L.M. Castro, R.M. Quinta-Ferreira, Phenolic wastewaters treatment by electrocoagulation process using Zn anode, *Chem. Eng. J.* 275 (2015) 331–341.
- [28] Y. Meas, J.A. Ramirez, M.A. Villalon, T.W. Chapman, Industrial wastewaters treated by electrocoagulation, *Electrochim. Acta* 55 (2010) 8165–8171.
- [29] D. Valero, J.M. Ortiz, V. García, E. Expósito, V. Montiel, A. Aldaz, Electrocoagulation of wastewater from almond industry, *Chemosphere* 84 (2011) 1290–1295.
- [30] K. Bani-Melhem, E. Smith, Grey water treatment by a continuous process of an electrocoagulation unit and a submerged membrane bioreactor system, *Chem. Eng. J.* 198–199 (2012) 201–210.
- [31] D.R. Manenti, A.N. Módenes, P.A. Soares, F.R. Espinoza-Quiñones, R.A.R. Boaventura, R. Bergamasco, V.J.P. Vilar, Assessment of a multistage system based on electrocoagulation, solar photo-Fenton and biological oxidation processes for real textile wastewater treatment, *Chem. Eng. J.* 252 (2014) 120–130.
- [32] D.D. Nguyen, H.H. Ngo, Y.S. Yoon, A new hybrid treatment system of bioreactors and electrocoagulation for superior removal of organic and nutrient pollutants from municipal wastewater, *Bioresour. Technol.* 153 (2014) 116–125.
- [33] C.H. Neoh, Z.Z. Noor, N.S.A. Mutamim, C.K. Lim, Green technology in wastewater treatment technologies: Integration of membrane bioreactor with various wastewater treatment systems, *Chem. Eng. J.* 283 (2016) 582–594.
- [34] A.D. Eaton, M.A.H. Franson, Standard Methods for the Examination of Water & Wastewater, American Public Health Association, 2005.
- [35] P. Cañizares, M. Carmona, J. Lobato, F. Martínez, M.A. Rodrigo, Electrodeposition of aluminum electrodes in electrocoagulation processes, *Ind. Eng. Chem. Res.* 44 (2005) 4178–4185.
- [36] A.P. Annachatre, Anaerobic treatment of industrial wastewaters, *Resour. Conserv. Recycl.* 16 (1996) 161–166.
- [37] R.S. Oremland, B.F. Taylor, Sulfate reduction and methanogenesis in marine sediments, *Geochim. Cosmochim. Acta* 42 (1978) 209–214.
- [38] N. Amaral-Silva, R.C. Martins, C. Paiva, S. Castro-Silva, R.M. Quinta-Ferreira, A new winery wastewater treatment approach during vintage periods integrating ferric coagulation, Fenton reaction and activated sludge, *J. Environ. Chem. Eng.* 4 (2016) 2207–2215.
- [39] D. Oumar, D. Patrick, B. Gerardo, D. Rino, B.S. Ihsen, Coupling biofiltration process and electrocoagulation using magnesium-based anode for the treatment of landfill leachate, *J. Environ. Manage.* 181 (2016) 477–483.