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Removal of volatile fatty acids and ammonia recovery from instable anaerobic digesters with a microbial electrolysis cell

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ABSTRACT

Continuous assays with a microbial electrolysis cell (MEC) fed with digested pig slurry were performed to evaluate its stability and robustness to malfunction periods of an anaerobic digestion (AD) reactor and its feasibility as a strategy to recover ammonia. When performing punctual pulses of volatile fatty acids (VFA) in the anode compartment of the MEC, simulating a malfunction of the AD process, an increase in the current density was produced (up to 14 times, reaching values of 3500 mA m^{-2}) as a result of the added chemical oxygen demand (COD), especially when acetate was used. Furthermore, ammonium diffusion from the anode to the cathode compartment was enhanced and the removal efficiency achieved up to 60% during daily basis VFA pulses. An AD-MEC combined system has proven to be a robust and stable configuration to obtain a high quality effluent, with a lower organic and ammonium content.

Keywords

Microbial Electrolysis Cell (MEC), Anaerobic digestion, Ammonia recovery, System stability, Volatile fatty acids (VFAs).

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1. Introduction

Livestock manure can be a source of energy and nutrients if managed and processed properly. Anaerobic digestion (AD) is a biological process which converts organic substrates in a mixture of gases (biogas) –mainly methane and carbon dioxide. This energy recovering technology is well established in terms of performance, is technically and economically feasible, and is widely used to treat various kinds of wastes (Angenent et al., 2004). However, this technology presents some drawbacks. In the first place, AD does not modify total N content of digestates, and thus when it is applied to livestock manure it needs to be combined with other processes for N removal or recovery to avoid effluent management constrains, such as chemical precipitation of ammonium and phosphate as struvite (Cerrillo et al., 2015), ammonia stripping and its subsequent absorption in an acid solution (Laureni et al., 2013) or thermal concentration of the digestate (Bonmatí et al., 2003). In the second place, the process can become instable by organic overload or inhibited by several substances that may be present in the waste stream, such as long chain fatty acids (Palatsi et al., 2009), ammonia (Yenigün and Demirel, 2013), sulphide, light metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+} and Al^{3+}), heavy metals and organic compounds such as chlorophenols or halogenated aliphatic compounds (Chen et al., 2008). Reactor inhibition caused by the accumulation of these substances will be indicated by reduced biogas production and/or biogas methane content, and accumulation of volatile fatty acids (VFA), such as acetate, propionate or butyrate, that may led to reactor failure. So it is interesting to find out new technologies that could keep effluent quality within the desired limits when combined with AD under unstable conditions.

Bioelectrochemical systems (BES), such as Microbial Electrolysis Cell (MEC), that use microorganisms attached to one or both bioelectrode(s) in order to catalyse oxidation and/or reduction reactions, can also be coupled to AD in order to improve its performance and effluent quality (Cerrillo et al., 2016). BES offer some advantages over AD as they perform properly at low substrate concentration levels. Combining AD and MEC is a new processing strategy aiming to recover energy and nitrogen simultaneously. On the one hand, ammonium can be removed and recovered, since it is transferred through the cation exchange membrane from the anode to the cathode compartment where it can be recovered (Cerrillo et al., 2016; Kuntke et al., 2014; Sotres et al., 2015; Zhang et al., 2013). And on the other hand, this system can produce additional energy and polish the AD effluent, especially when malfunction of the AD system is produced due to organic overloads or inhibition process, attaining a more stable and robust performance.

The combination of BES and AD has been previously studied, although using Microbial Fuel Cell (MFC) mode and with the objective of polishing the digestate, such as the effluent of a two-stage biogas process at low organic loading (Fradler et al., 2014), digested landfill leachate (Tugtas et al., 2013) or digested wastewater from potato-processing industries (Durruty et al., 2012). Also the long-term performance of sludge treatment has been examined in an MFC operated for almost 500 days (Ge et al., 2013). Another MFC has been coupled with a hydrogen production fermentor (Sharma and Li, 2010). It has also been described an up-flow anaerobic sludge blanket reactor-microbial fuel cell-biological aerated filter (UASB-MFC-BAF) integrated system for simultaneous bioelectricity generation and molasses wastewater treatment (Zhang et al., 2009). Finally, a previous work has compared the treatment of digested pig slurry under

MFC and MEC mode (Cerrillo et al., 2016). Other studies have focused on the assessment of VFA removal using synthetic mediums (Chae et al., 2009; Yang et al., 2015). However, VFA removal from complex substrates may show a different behaviour and kinetic, so more research is needed.

A deep assessment of BES performance against an AD destabilization has not been undertaken, neither its influence in ammonia recovery. Stability can be defined by the concepts of resistance (ability of a system to resist disturbance) and resilience (rate of recovery of a system after a disturbance) (Hashsham et al., 2000). Different studies have found a positive correlation between biodiversity and stability when working with activated sludge (Saikaly and Oerther, 2010). But stability has found to be best correlated not to population diversity *per se* but to functional redundancy (Briones and Raskin, 2003). Methanogens are represented by a low diversity compared to the more diverse fermentative bacteria (Saikaly and Oerther, 2010). In AD reactors, the lack of functional redundancy of the methanogenic group suggests that they may be less functionally stable to toxic shock loading. In BES, microorganisms develop into a biofilm on electrodes, which confers their good resistance to toxic substances and environmental fluctuations (Borole et al., 2011) and makes the integration of BES with AD an attractive synergic mode (Zhang et al., 2009).

The main aim of this study is to assess the stability and robustness of continuous MEC operation in combination with AD, and its feasibility as a strategy to recover ammonia. MEC response to punctual and sustained organic overloads when fed in continuous with AD effluent as a result of AD failure was evaluated, regarding resistance and resilience against the perturbation, VFA removal and its capacity to

absorb the higher organic load to increase current density production and ammonia removal.

2. Materials and methods

2.1 Experimental set-up

The MEC reactor consisted of a two chamber cell constructed using methacrylate (0.5 L each compartment). The anode of this MEC had been inoculated from a mother MFC, and was operated previously in batch mode with digested pig slurry, as described elsewhere (Cerrillo et al., 2016). A cation exchange membrane (CEM, dimensions: 14 x 12 cm; Ultrex CMI-7000, Membranes International Inc., Ringwood, NJ, USA) was used to separate the anode and cathode compartments. The anode was a carbon felt (dimensions: 14 x 12 cm; thickness: 3.18 mm; Alfa Aesar GmbH and Co KG, Karlsruhe, Germany); and a 304 stainless steel mesh was used as cathode (dimensions: 14 x 12 cm; mesh width: 150 μm; wire thickness: 112 μm; Feval Filtros, Spain). The anode was connected to the cathode through a potentiostat (VSP, Bio-Logic, Grenoble, France) in a three electrode mode for data monitoring and poising of the anode potential (working electrode) at 0 mV. An Ag/AgCl reference electrode (Bioanalytical Systems, Inc., USA) was inserted in the anode compartment (+197 mV vs. SHE, all potential values in this paper are referred to SHE). A personal computer connected to the potentiostat recorded electrode potentials and current every 5 min using EC-Lab software V10.32 (Bio-Logic, Grenoble, France).

Digested pig slurry was used as feeding solution in the anode compartment. The digestate was obtained from a mesophilic AD plant with a hydraulic retention time (HRT) of 40 days (Vila-Sana, Lleida, Spain), previously filtered through a stainless steel sieve to remove particles larger than 125 μm and diluted with tap water to obtain

the desired COD. Table 1 shows the main characteristics of the feeding solution. The feeding solution for the cathode chamber contained NaCl 0.1 g L^{-1} (in deionised water). The solutions of both the anode and the cathode compartment were fed in continuous with a pump working at 16.4 mL h^{-1} and mixed by recirculating them with an external pump.

2.2 Reactor operation

The MEC was operated in continuous for 110 days with an HRT of 30 h. In Phase 1, the MEC was fed for 10 days with the digestate to evaluate its performance under a stable operation of the AD reactor, with an organic loading rate (OLR) of 18.24 g COD L^{-1} d^{-1}. In Phase 2, in order to simulate an overload episode of the AD system and to study VFA degradation dynamics in the MEC, a series of pulses of diverse VFA were performed in the anode compartment in duplicate, increasing the added COD in each series, while in Phase 3 the pulses were of mixed VFA (Table 2). Each pulse was performed once the current density had returned to basal levels. Finally, in Phase 4, a daily pulse of mixed VFA (acetate, propionate and butyrate, as specified in Table 2) was applied for 5 days to the MEC cell for 2 weeks, simulating a long period of malfunction of the AD reactor. VFA concentration in the anode compartment after each pulse reached values of 1500-2000 mg L^{-1}, which are typical values for inhibited AD, since under stable operation total VFA concentration is normally under 500 mg L^{-1} as acetic acid (Amani et al., 2010). All assays were performed at room temperature (~ 23 ºC). Samples were taken from the anode and the cathode compartments prior to the pulse, and at time 1, 7, 24 and 48 h after the pulse.

2.3. Analytical methods and calculations

The bulk solution pH in each experiment was measured using a CRISON 2000 pH electrode. Chemical oxygen demand (COD), ammonium N-NH_4^+, alkalinity (Alk) and pH were determined according to Standard Methods 5220 (APHA, 1999). Ammonium (N-NH_4^+) was analysed by a Büchi B-324 distiller, and a Metrohm 702 SM autotitrator. Volatile fatty acids (VFAs) were quantified using a VARIAN CP-3800 (Varian, USA) gas chromatograph equipped with a flame ionization detector (FID). Anion concentration (Cl^-, NO_3^-, NO_2^- $H_2PO_4^{3-}$, SO_4^{2-}) was measured by ionic chromatography (IC) with an 861 Advanced Compact IC (Metrohm, Switzerland) using a Metrosep A Supp 4-250 (Metrohm, Switzerland) column and a CO_2 suppressor. Cations (Na^+, K^+, Ca^{+2}, Mg^{+2}) were also measured by a 790 Personal IC (Metrohm, Switzerland) and a Metrosep C2 column (Metrohm, Switzerland). Samples were previously diluted and filtrated with nylon (0.45 mm) and BonElut JR C18 micro filters (Varian, USA).

Methane production in the MEC was calculated through the determination of dissolved methane in solution, as described elsewhere (Cerrillo et al., 2016). Methane in the samples was determined using a VARIAN CP-3800 (Varian, USA) gas chromatograph equipped with a thermal conductivity detector (TCD).

Ammonium removal efficiency as well as COD removal efficiency were calculated based on the difference between influent and effluent concentrations divided by the influent concentration.

The current density (A m^{-2}) was obtained as the quotient between the current measured by the potentiostat, I (A) and the area of the anode, A (m^2). The Coulombic

efficiency (CE), based on current generation and the amount of COD removal during MEC operation, was calculated as:

$$CE = \frac{M\ I}{FbqΔCOD} \quad (1)$$

where M is the molecular weight of the final electron acceptor, I is the current (A), F is Faraday's constant, b is the number of electrons transferred per mole of O_2, q (L s^{-1}) is the volumetric influent flow rate and ΔCOD is the difference between the influent and effluent COD (g L^{-1}).

Resilience was used as a measure of system stability, and was calculated as the time taken for VFA concentration to recover basal levels.

Data were analysed using one-way analysis of variance (ANOVA). Whenever significant differences of means were found, the Tukey test at a 5% significance level was performed for separation of means. Statistical analysis was performed using the R software package (R project for statistical computing, http://www.r-project.org).

2.4. Anaerobic biodegradability assay

The anaerobic biodegradability of the digested pig slurry (substrate) was evaluated in serum bottles (120 mL) in duplicate (Angelidaki et al., 2009). Anaerobically digested sludge from a mesophilic lab-scale anaerobic digester was used as inoculum. The serum bottles were filled with 50 mL of a solution composed of the inoculum (5 g_{VSS} L^{-1}), substrate (5 g_{COD} L^{-1}), macronutrients, micronutrients and bicarbonate (1 $g_{NaHCO3-}$ $g_{CODadded}^{-1}$). A control duplicate without medium was included

in the setup. The bottles were sealed with rubber stoppers and capped with aluminium crimp caps. The headspace was purged with N_2 in order to remove O_2. The bottles were incubated at 35 ºC for 41 days. Methane production was monitored by periodically taking a gas sample (0.2 mL) from the head space with a gas-tight syringe and analysing the gas composition by gas chromatography.

3. Results and discussion

3.1. Stable feeding with digested pig slurry (Phase 1)

During this phase the MEC was fed with digested pig slurry and showed a stable performance in current density (Figure 1), achieving a 100% reduction in VFA (on average 110 mg L^{-1} acetic acid were present in the influent and it was not detected in the effluent). The average COD removal was of 12.21±1.77%, indicating that mainly low biodegradable COD was available in the digestate. The anaerobic biodegradability assay performed in mesophilic conditions with the same digested pig slurry which was fed to the MEC showed an anaerobic biodegradability of 33% (data not shown). Taking this value as a reference, the MEC was able to remove 37% of the biodegradable organic matter which was present in the digested pig slurry, concomitant to an ammonium removal efficiency of 11.81±1.36% (3.73±0.51 g N m^{-2} d^{-1}). The current density produced was of 425±77 mA m^{-2}. The average CE was of 3.52% (10.67% if taking into account only the biodegradable COD), and just 0.97% of the removed COD was converted into methane (the anodic effluent contained 11.40±0.72 mg_{CH4} L^{-1}). These results are in accordance with the values that have been obtained in previous studies. Ge et al. (2013) obtained 36.2±24.4% COD removal and 2.6±1.4% CE with an MFC treating digested sludge, although with a much longer HRT (9 days) and an influent

COD of 16.7±11.4 g L^{-1}. Recent work with a MEC fed with digested pig slurry (8 g COD L^{-1} and 872 mg N-NH_4^+ L^{-1}) in discontinuous mode achieved a maximum peak of 700 mA m^{-2} when poising the anode at 0 mV, with a COD removal efficiency of nearly 20% and an ammonium removal efficiency of around 30% in 48 h assays (Cerrillo et al., 2016). Longer HRT and lower COD and ammonium concentration may have favoured these higher removal efficiencies. Higher ammonium removal efficiencies of around 30% (171.4 g N m^{-2} d^{-1}) have been reported in another study using a MEC fed with diluted urine, which may have been obtained thanks to the high current densities achieved of 14.64±1.65 A m^{-2} (Kuntke et al., 2014), which were nearly 35 times higher than the ones described in the present study, and a shorter HRT of 2 h.

The pH of the effluent of the anode compartment was of 7.8±0.1, thus slightly lower than the pH of the influent (8.2±0.1). The buffering capacity of the anolyte (digested pig slurry; alkalinity 13.8 g_{CaCO3} L^{-1}) avoided a higher decrease in the pH of the anode compartment, despite the acidification due to cation transport to the cathode compartment and proton accumulation in the anode (Rozendal et al., 2008). Regarding the pH of the cathode effluent, it was of 10.1±0.1, a very convenient pH for ammonia recovering, as it can drive ammonium to ammonia gas and favour a subsequent stripping and absorption process (Cord-Ruwisch et al., 2011; Kim et al., 2008; Kuntke et al., 2012; Sotres et al., 2015). The increase of pH in the cathode compartment was favoured since no buffer solution was used.

3.2. Punctual VFA pulses (Phase 2)

The response of the MEC after the pulses of acetate was an immediate increase in current density, with a peak of between 1300 and 1700 mA m^{-2} for the 250 mg pulses and between 2100 and 2600 mA m^{-2} for the 500 mg pulses; and a later decrease of the

current density concomitant with acetate removal, achieving the total degradation in 24 h and 48 h for the 250 and 500 mg pulses, respectively (Figure 2a). Current density returned to levels of around 500 mA m^{-2}, similar to those obtained in Phase 1, demonstrating a high resilience to perturbation by VFA accumulation. The amount of charge produced, calculated by integrating the area under the current (A) peak, resulted in 0.65±0.03 and 1.62±0.15 mmol of electrons, equivalent to 1.94 and 2.42% of the COD added with the 250 and 500 mg pulses, respectively. Methane production increased slightly during acetate pulses, with a concentration of 12.60±2.34 mg_{CH4} L^{-1} and 14.45±2.53 mg_{CH4} L^{-1} in the anodic effluent for the 250 and 500 mg pulses, respectively, although this difference was not statistically significant. A slight increase in ammonium removal was also observed, from a level of 15% before the pulse to around 20% after the pulse, in response to the increase of electron transport through the external circuit. As a result of the increase of current density, the pH of the cathode compartment was also increased during current peaks, achieving a pH of 11 during 250 mg pulses and even above 12 during the 500 mg ones. The pH of the anode effluent oscillated between 7 and 8, which is an optimum range for microbial activity.

The response to propionate pulses was less intense than the one obtained with the acetate pulses: the increase in current density was observed with a slight delay, and the peak achieved 1000 mA m^{-2} (Figure 2b). After 24 h a level of 200 mg L^{-1} of propionate still remained in the effluent, and a small amount of acetate was detected (around 100 mg L^{-1}). Although the electrons that could potentially be delivered through propionate degradation were 1.4 fold higher than those available in the 500 mg acetate pulse (each g of acetate will produce 135.5 mmols of electrons in MEC's anode and 1 g of propionate will release 191.6 mmols of electrons), the amount of charge produced

resulted in 0.45±0.05 mmols of electrons, equivalent to 0.47% of the COD added with the pulse. A recent study has revealed simultaneous multiple paths of electron flow to current during propionate oxidation in the anode of MECs, either via acetate/H_2 or via acetate/formate (Hari et al., 2016). However, the low conversion of propionate to electric current in this study could be explained because acetate was the only VFA present in the influent of the MEC and thus the development of propionate oxidizing populations, probably different to acetate oxidizing populations (Boschker et al., 2001), has not been favoured. Methane production was not statistically different to acetate pulses, with a concentration of 15.42±1.82 mg_{CH4} L^{-1} in the anodic effluent. As the peak current was less intense, the increase of pH in the cathode effluent was also moderate, achieving a maximum pH of 11.5. Ammonium removal was not enhanced during propionate pulses, since it was similar to the removal efficiency obtained in Phase 1.

Finally, the pulses of butyrate showed an increase in current density with a wider peak than the ones obtained with the acetate pulses, and a maximum of nearly 2500 mA m^{-2} (Figure 2c). Butyrate concentration in the anode effluent was of about 70 mg L^{-1} within 24 h, and acetate increased to levels between 200-360 mg L^{-1} during the peaks and decreased to basal levels after 24h. The presence of acetate, produced by butyrate degradation, explains the width of the current peak, and suggests the existence in the anode of a microbial population more efficient in the oxidation of butyrate and acetate than of propionate. The potential amount of charge that could be produced from the butyrate pulse was 1.7 fold higher than in the 500 mg acetate pulse, although the area under the peak corresponded with 1.95±0.01 mmol of electrons, only 1.2 fold higher, and 1.72% of the electrons provided by the pulse. Methane concentration in the anodic effluent 7 h after the pulse achieved levels of 20 mg_{CH4} L^{-1}. Furthermore, in response to

a higher level of current production, cathode pH remained near 12 during both butyrate pulses. The pH of the node, as in the preceding pulses, remained between 7 and 8. The ammonium removal efficiency was enhanced during the second butyrate pulse, concomitant to a higher and wider peak of current density, achieving nearly 28%.

From those results it can be said that the MEC has shown a high resilience against VFA increase in the influent, since the high levels of VFA have been removed, within the concentrations tested, and the effluent concentration returned to the initial level in about 48 h. Furthermore, each of the three VFA assayed had positive effect on power density. However, as shown here and consistent with previous results, acetate was the preferred substrate for electricity generation in MFC/MEC, and microbial community was less efficient in converting propionate to energy, as other studies have shown (Choi et al., 2011; Yang et al., 2015). Acetate can be directly consumed for electricity generation; however, long-chained VFAs must first be converted into acetate. In a previous study, MFC in fed batch mode with synthetic medium with the same VFA as assayed here showed that CE and power output varied with the different substrates. The acetate-fed-MFC showed the highest CE (72.3%), followed by butyrate (43.0%) and propionate (36.0%) (Chae et al., 2009). In a batch single-chambered MFC, power generated when feeding with acetate was up to 66% higher than that obtained when feeding with butyrate (Liu et al., 2005). A better performance in a MFC fed with acetate was obtained respect the ones fed with propionate or butyrate. For the same organic loading rate, the electric current generated with propionate or butyrate was half the produced with acetate (Freguia et al., 2010).

3.3. Punctual mixed VFA pulses (Phase 3)

Current density profiles of the pulses of mixed VFA are shown in Figure 3. When a pulse of acetate and propionate was applied (500 mg each one), the maximum current density achieved was between 2000 and 3000 mA m^{-2}, quite similar to the one obtained when only acetate was applied, although the base of the peak was wider. Both VFA were removed at a similar rate, being undetectable 48 h after the pulse, when the current density decreased to values below 500 mA m^{-1}. The amount of charge produced did not correspond to the addition of the charge produced during the pure VFA pulses in Phase 2, but was a value very similar to the one obtained with the pulse of only acetate (1.70±0.21 mmol of electrons, 1.05% of the potential charge added with the pulse). Methane concentration in the anodic effluent was of 7.91±2.58 mg_{CH4} L^{-1}, significantly lower to the one obtained with pure 500 mg acetate pulses, although the recovery of electrons was lower. The pH of the cathode effluent increased again up to 12, while the pH of the anode effluent decreased but was always above 7. The ammonium removal followed the current density profile, being 30% the maximum removal efficiency.

Regarding the mixed VFA pulses of acetate, propionate and butyrate, Figure 3b shows that the current density peaks were between 3000 and 3500 mA m^{-2}, and that the bases of the peaks were the widest ones among all the pure and mixed VFA pulses performed. Current density decreased sharply when VFA were totally removed, between 48 and 55 h after the pulse, and returned to levels below 500 mA m^{-2}, similar to those obtained in Phase 1. The amount of charge produced was of 2.65±0.19 mmol of electrons, a 1.39% of the potential charge added with the pulses. As in the previous mixed VFA pulses, methane concentration in the anodic effluent (10.04±3.02 mg_{CH4} L^{-1}) was not statistically different to that obtained with pure VFA. Showing again a very

similar behaviour to the mixed VFA pulses of acetate and propionate, the pH of the cathode and the anode increased up to 12 and decreased down to nearly 7, respectively. The ammonium removal efficiency increased to levels of 35%.

These results show that when mixed VFA pulses are applied, a high resilience is shown again by the MEC, since VFA and current density levels return to the initial ones in about 48 h. It has also been observed that the efficiency of the MEC in the electricity conversion is lower when mixed VFA are applied than with pure VFA. This is in agreement with the results reported in previous studies. When food wastes were used as feedstock in a MFC, it was found that the co-existence of various VFA slowed the removal of each VFA, which indicated that anodic microbes were competing for the different substrates. Furthermore, the degradation rate of butyrate increased when short VFAs were absent in the anode chamber, indicating that these readily degradable short compounds inhibited microbial activity on large VFAs (Choi et al., 2011). Teng et al. (2010) found that although both acetate and propionate contributed positively to the power density, they had antagonistic effects when they were mixed together. Similar antagonistic effects were also obtained in that study for acetate–butyrate and propionate–butyrate, and the increase or decrease of the power density depended on the relative proportion of each VFA in the mixture.

3.4. Continuous daily base mixed VFA pulses (Phase 4)

During the mixed VFA daily base pulses performed in the MEC, power density was maintained on average between 1500 and 3000 mA m^{-2} (Figure 4). Acetate from the previous pulse had not been consumed when a new pulse was added (remaining around 1000 mg L^{-1}), but after 3 days, before starting the second series of pulses all

VFA had been removed. During the second series, the peaks of acetate were lower than in the first series.

Therefore, the MEC was able to maintain a stable production of current and reduce acetate concentration, avoiding VFA accumulation. Furthermore, methane production remained in the lowest levels among the different punctual pulses performed, with an average concentration in the anodic effluent of 5.09±1.45 mg_{CH4} L^{-1}. During the daily pulses, the pH of the cathode increased and remained between 12-12.5. The pH of the anode was stable around 7-8, showing a slight oscillation in the later pulses performed, decreasing down to 6.5 but recovering to values higher than 7 few hours after the pulse. Furthermore, the ammonium removal increased during the series of pulses to a level of 40%, achieving in the second series values of around 60%. These values are higher than those obtained in previous studies which achieved an ammonium removal efficiency of 30%, but with 10 fold higher current densities (Kuntke et al., 2014).

Sharma et al. (2014) proposed some general guidelines to meet robustness with electroactive biofilms. One of them was that electroactive biofilm should exhibit preservation of the predominant electrochemical mechanisms and metabolic constructs by which a targeted outcome was achieved (e.g. generation of electric current, a set of organic chemicals, recalcitrant COD removal, denitrification, metal reduction, etc.) after scenarios of metabolic disturbances common to BES (e.g. fluctuations in potential, pH, temperature, conductivity, substrate concentration and composition, power supply instabilities/interruptions, flow rate, dissolved oxygen). The MEC evaluated in this study has proven to be a robust system, showing a high resistance to organic overloads

and also a high resilience, since after both punctual and daily VFA pulses the system has been able to recover its performance in less than 48 h after the stress.

A previous study, focused on evaluating an AD-MFC hybrid system stability using a high acetic load as disturbance, reported that the hybrid system did not have increasing resilience compared to the solitary systems. However, since the low pH had a relatively delayed effect on the MFC compared to the AD, the energy output indeed was more stable in the hybrid system (Weld and Singh, 2011). By contrast, the objective of this paper has been to assess the stability of an AD-MEC system during a range of less severe stresses, showing that using a MEC as a post-treatment of AD can improve the quality of the effluent during AD malfunction, both at high levels of VFA and ammonia, while recovering energy.

4. Conclusions

The MEC removed high levels of VFA from AD effluents, showing as a useful technology to correct possible malfunction of AD reactors. During punctual pulses of VFA, ammonium diffusion from the anode to the cathode compartment was enhanced and the removal efficiency achieved up to 60% during daily basis pulses, since electron transport is directly related to cation transport through the CEM membrane. An AD-MEC combined system has proven to be a robust and stable configuration to recover energy and obtain a high quality effluent, with a lower organic and ammonium content.

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Figure captions

Figure 1 Current density during Phase 1, of stable feeding with digested pig slurry.

Figure 2 Current density, VFA concentration, ammonium removal and anode and cathode pH obtained in Phase 2 during the VFA pulses of (a) 250 and 500 mg of acetate, (b) 500 mg of propionate and (c) 500 mg of butyrate. Arrows show when each pulse was performed.

Figure 3 Current density, VFA concentration, ammonium removal and anode and cathode pH obtained in Phase 3 during the mixed VFA pulses of (a) 500 mg of acetate and 500 mg of propionate and (b) 1000 mg of acetate, 200 mg of propionate and 85 mg of butyrate. Arrows show when each pulse was performed.

Figure 4 Current density, VFA concentration, ammonium removal and anode and cathode pH obtained in Phase 4, during daily pulses of 1000 mg of acetate, 200 mg of propionate and 85 mg of butyrate. Arrows show when each pulse was performed.

Tables

Table 1. Characterization of digested pig slurry and the final solution used as feeding in the MEC.

Parameter	Digested Pig Slurry	Digested Pig Slurry MEC influent*
pH (-)	8.4	8.2
COD (mg O_2 kg^{-1})	173 369	23 170
N-NH_4^+ (mg L^{-1})	4 438	2 190
TS (%)	8.39	1.44
VS (%)	6.10	0.90
Acetate (mg L^{-1})	261	110
Alkalinity (g_{CaCO3} L^{-1})	13.8	-
NH_4^+ (mg L^{-1})	3 806	1 827
Na^+ (mg L^{-1})	1 014	694
Mg^{2+} (mg L^{-1})	n.d.	n.d.
Ca^{2+} (mg L^{-1})	3 566	1 199
K^+ (mg L^{-1})	1 374	650
PO_4^{3-} (mg L^{-1})	184	n.d.
SO_4^{2-} (mg L^{-1})	3 463	972

* Digested pig slurry sieved 125 μm and diluted 50%

n.d: not detected

Table 2. Operational conditions for the MEC reactor during the series of VFA pulses.

Phase	Day	VFA addition (mg)			Added COD (mg)
		Acetate	Propionate	Butyrate	
1	1-10	0	0	0	-
2	11 and 12	250	0	0	267
	13 and 17	500	0	0	534
	19 and 20	0	500	0	757
	60 and 62	0	0	500	909
3	33 and 38	500	500	0	1291
	40 and 47	1000	200	85	1525
4	66 to 70 73 to 77	1000	200	85	1525

Figure 1

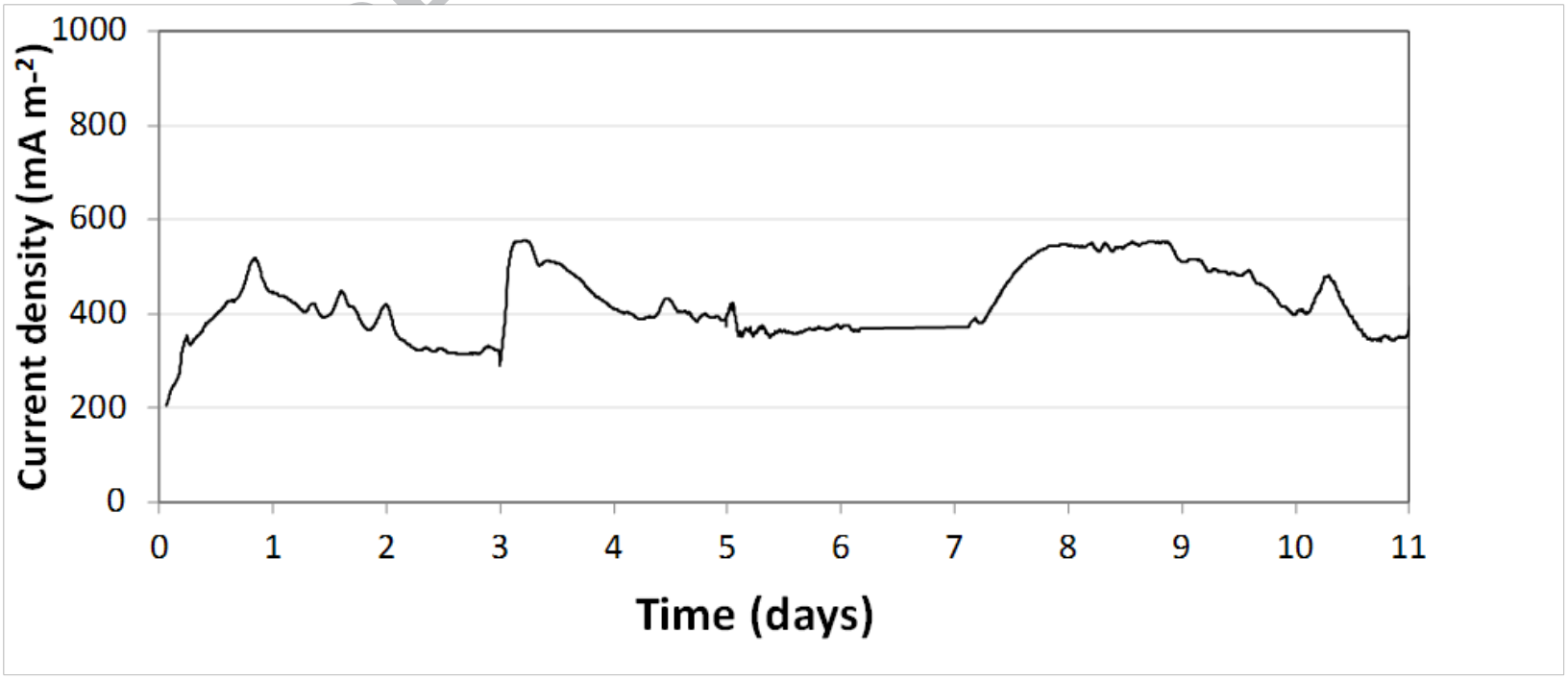


Figure 2

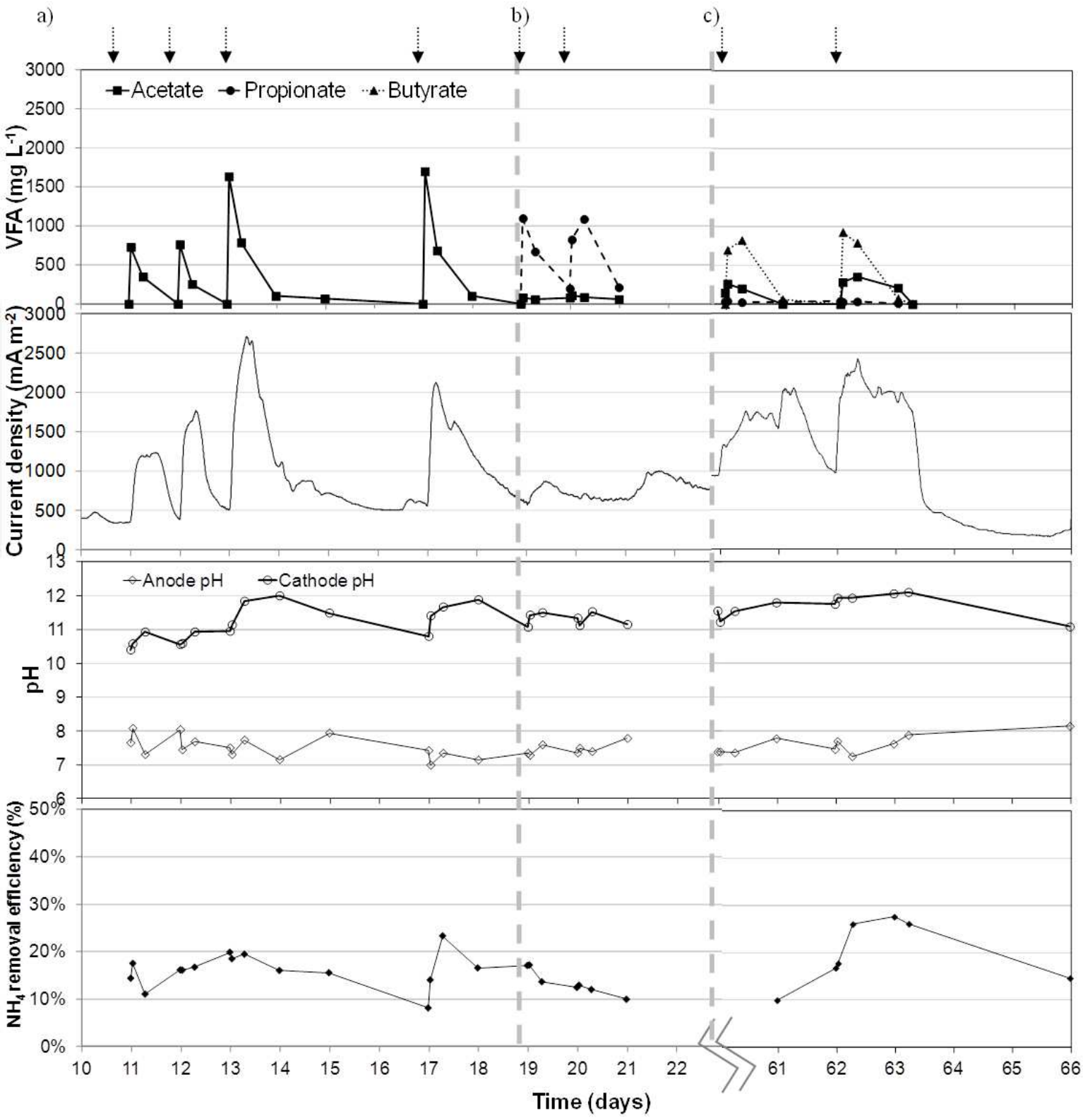


Figure 3

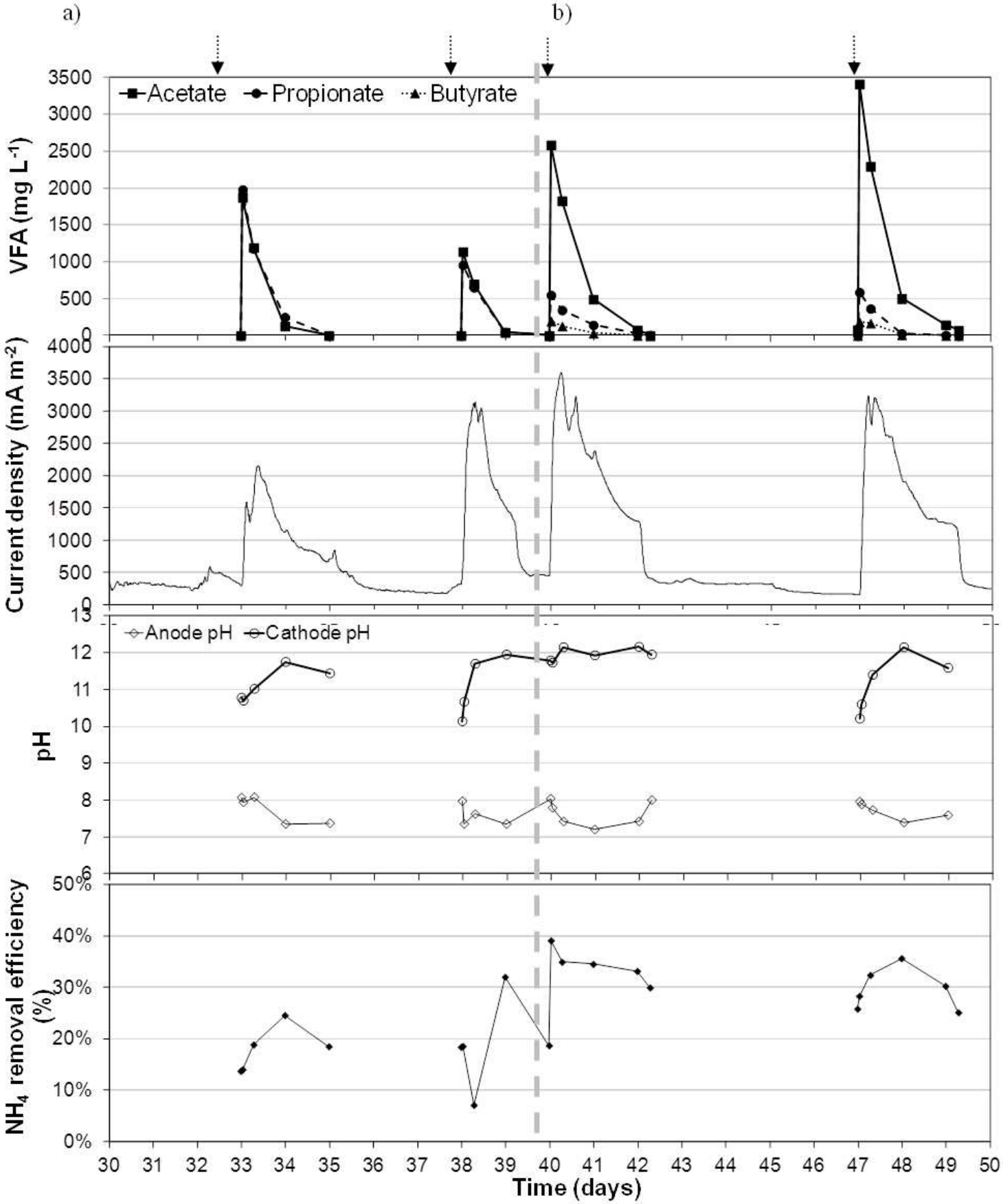
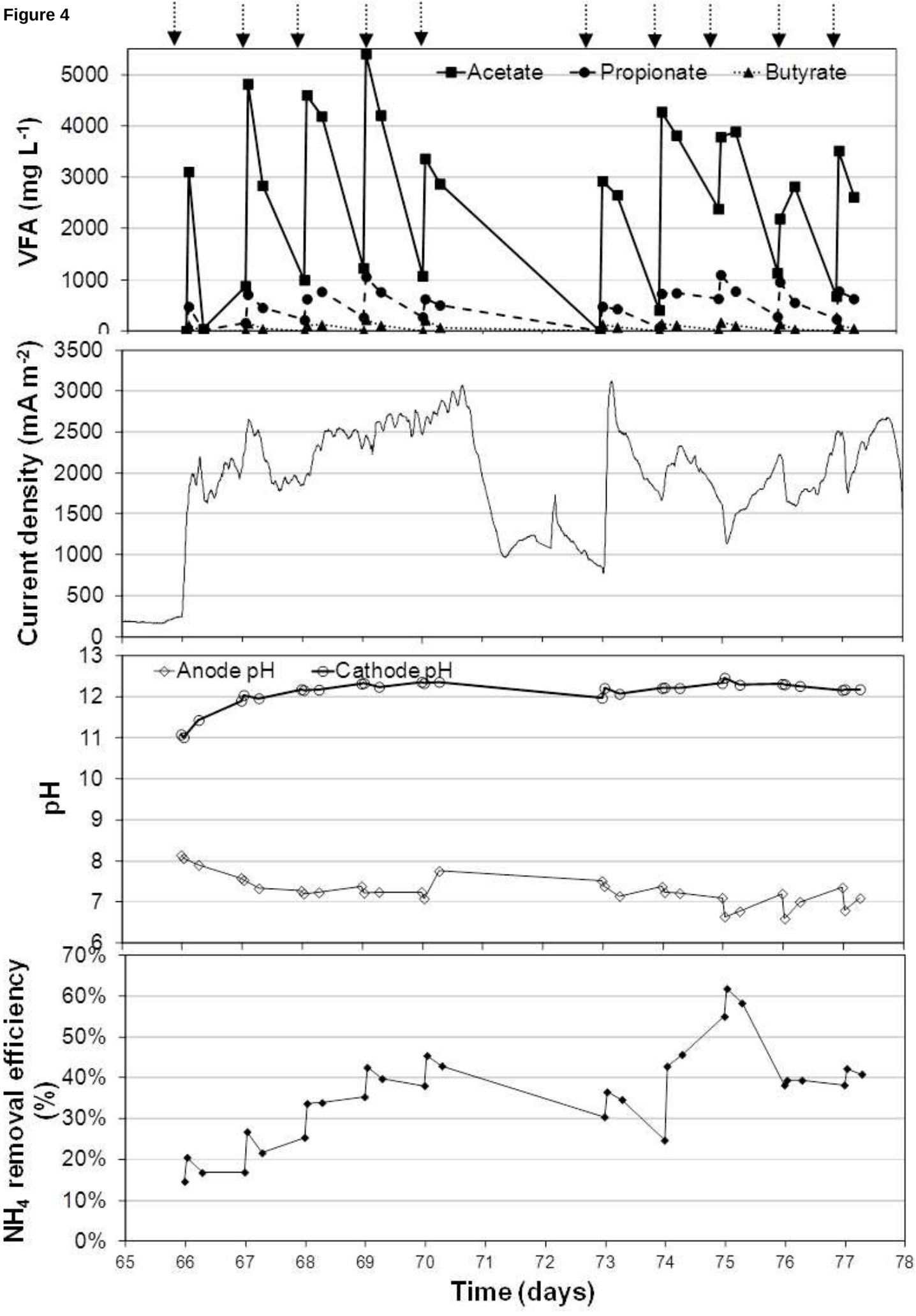
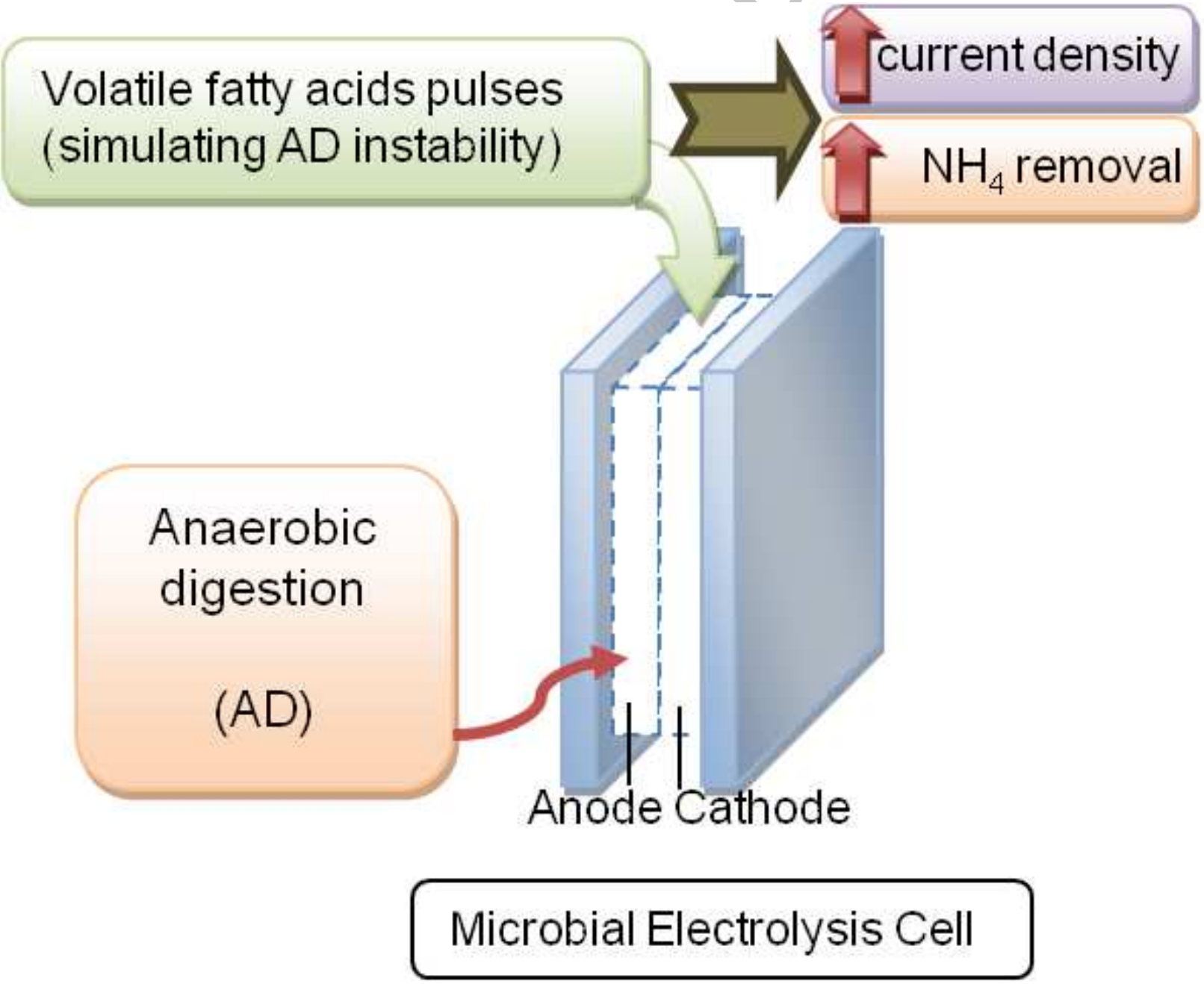


Figure 4


Acetate
Propionate
Butyrate
VFA (mg L-1)
Current density (mA m-2)
Anode pH
Cathode pH
pH
NH4 removal efficiency (%)
Time (days)


Volatile fatty acids pulses
(simulating AD instability)
current density
NH_4 removal
Anaerobic
digestion
(AD)
Anode
Cathode
Microbial Electrolysis Cell

- MEC is a useful technology to correct AD instability, removing VFA and ammonia.
- Acetate and butyrate pulses produced higher current densities than propionate ones.
- Ammonium removal efficiency achieved 60% during VFA mix daily basis pulses.
- The MEC treating AD effluents showed as a resistant and resilient system.