

1 A critical evaluation of the pH split and associated effects in 2 bioelectrochemical processes

3 Marco Zeppilli¹, Paola Paiano¹, Cesar Torres², Deepak Pant³

4

5 ¹ Chemistry Department, University of Rome Sapienza, Piazzale Aldo Moro 5, 00185 Rome (Italy)

6 ² School for Engineering of Matter, Transport and Energy, Arizona State University 501 E Tyler Mall, Tempe,
7 Arizona 85287, United States

8 ³ Separation & Conversion Technology, Flemish Institute for Technological Research (VITO), Boeretang 200,
9 2400 Mol (Belgium)

10

11 **Abstract**

12 Typical reactions in bioelectrochemical systems (BESs) promote the phenomenon of the pH
13 split between anode and cathode. The pH split results in an undesirable phenomenon which
14 has stimulated several technological solutions to limit its effects, particularly for energy-
15 producing bioelectrochemical systems (BESs). On the other hand, several applications of
16 energy-consuming BESs exploited the pH split to integrate different operations using the
17 bioelectrochemical reactions. Those additional operations, which are directly related to the
18 electric field generated by the bioelectrochemical interphases, include target products
19 extraction, concentration, and recovery. This review offers a comprehensive overview of the
20 different bioelectrochemical applications in which the pH split is used for the integration of
21 bioelectrochemical reactions with products concentration and recovery. By discussing the
22 phenomenon of the pH split in BESs, this paper presents an alternative view to stimulate
23 new niches of applications for the bioelectrochemical processes.

24

25 **Keywords:** Bioelectrochemical systems, secondary Microbial Electrochemical
26 Technologies (METs), ammonia recovery, phosphorus recovery, biogas upgrading, water
27 softening

28 **1. Introduction: Ionic charge transport and pH split generation in bioelectrochemical**
29 **systems**

30 Bioelectrochemical systems (BESs) are unique systems which exploit the capability of
31 certain microorganisms to exchange electrons with solid electrodes through the mechanism
32 of extracellular electron transfer (EET) [1, 2]. The presence of an electroactive biofilm
33 growing on the electrode surface constitutes a (bio)electrochemical interphase or a
34 bioelectrode [3]. When the biofilm (electricigens) exchange electrons with an electron
35 acceptor, this interphase is called bioanode [4], or biocathode (electrotrophs) when the
36 electrode represents the electron donor in the process [5]. The exchange of electrons
37 between the electroactive microorganisms and the electrode material can be performed due
38 to the presence of specialized membrane proteins and their extensions [6-8] or indirectly
39 through mediators acting as electrons shuttles [9-11]. Commonly, a (bio)electrochemical
40 process is considered a redox reaction in separated phase, which allows the electrons
41 exchange through an electrical circuit, while ionic species must migrate between the anodic
42 and the cathodic chamber of the BESs [12-14].

43
44 According to the electroneutrality maintenance, the negative charge flow carried by the
45 electrons from the anode to the cathode was counterbalanced by the migration of ionic
46 species in the electrolytic solutions. The flux ($J_{mig,i}$) of positive or negative ionic species
47 involved in electroneutrality maintenance for the i ion, can be described by the Nernst-Planck
48 equation, shown here for the simplified case of no advection, as the sum of the diffusional
49 ($J_{diff,i}$) and migrational fluxes in one dimension flux:

50
$$J_i = J_{diff,i} + J_{mig,i} = -D_i \frac{\partial C_i}{\partial z} - \frac{z_i F}{RT} D_i C_i \frac{\partial V}{\partial z} \quad (1)$$

51 where,

52 D_i = diffusion coefficient of the ion i ($\text{cm}^2 \text{sec}^{-1}$)
53 C_i = concentration of the ion i (mmol cm^{-3}),

54 z = distance (cm)
55 F = Faraday constant (96,485 coulombs/mole)
56 R = ideal gas constant (8.314 J mol⁻¹ K⁻¹)
57 T = temperature (K)
58 z_i = charge of the ion i (dimensionless)
59 V = electric potential (V)

60 Each ion present in the medium contributes to this migration. According to the transference
61 number, the fraction of this contribution of migration flux for a specific ion is dependent on
62 its charge, concentration, and diffusion coefficient [12]:

63
$$t_i = \frac{J_{mig,i}}{J_{mig}} = \frac{|z_i|^2 D_i C_i}{\sum_k |z_k|^2 D_k C_k} \quad (5)$$

64 where J_{mig} refers to the total migration flux. In a conventional abiotic electrochemical
65 process, such as the water electrolysis, a high concentration of ionic species is used to
66 ensure a good conductivity (i.e. 10–33% KOH solution is used to obtain a conductivity of up
67 to 60 S/m in available water electrolyzers). In the BESs, the electrolytes are neutral solutions
68 optimized for the biofilm growth [15], which is however characterized by a low ionic
69 conductivity due the low tolerance of many microorganisms to high salinities [16-18]. Under
70 these conditions, the concentration of the proton is 10⁻⁴ mM, whereas other cations and
71 anions (e.g., Na⁺, K⁺, NH₄⁺, Ca²⁺, and Mg²⁺) are usually 10⁵ times more concentrated. This
72 leads to a variety of ions being transported through migration forces in BESs.

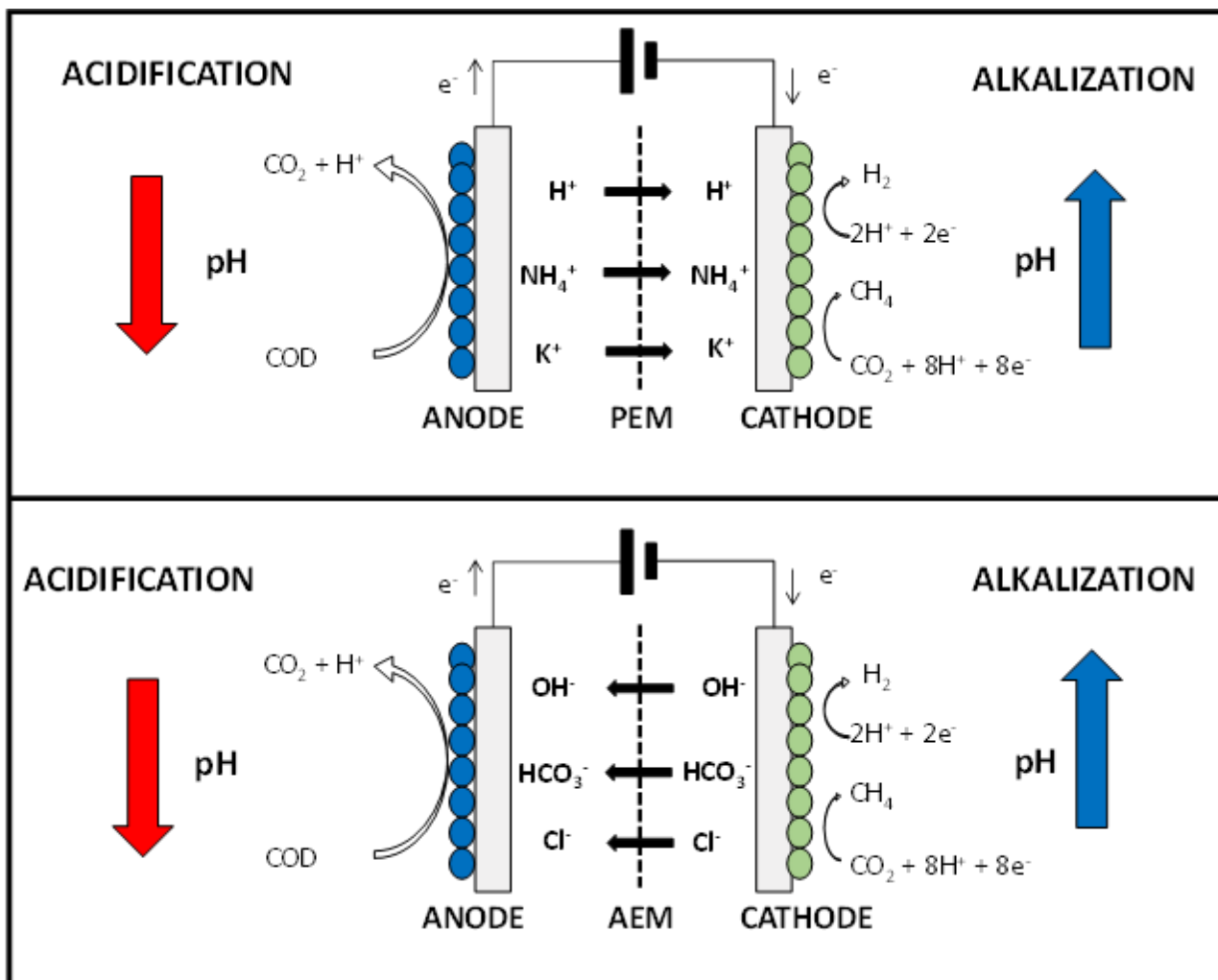
73 Different strategies can be adopted to guarantee the electroneutrality maintenance while
74 separating anode and cathode, which include the use of ion exchange membranes (IEM)
75 [19, 20], non-porous membrane for the selective transport of cations (cation exchange
76 membranes, CEM) [21], anions (anion exchange membranes, AEM) [22] or both cations
77 and anions (bipolar exchange membranes, BPM) [23]. Both CEMs and AEMs are
78 characterized by fixed charges that create a high selectivity for the respective charge it is
79 intended to transport. In other words, the transference number for counter ions is very low,
80 allowing a selective migration across the membrane. The permselectivity is the ion
81 selectivity between counter- and co-ions; it represents the most important property of IEMs

82 regulating the coulombic and energy efficiency of the electrochemical process.. In general,
83 the resistance of a IEMs depends on the chemical structure and its permselectivity [a].
84 Usually, for commercially available membranes, constituted by a homogeneous polymer,
85 resistivity (i.e. area resistance normalized by film thickness) is measured using a dilute NaCl
86 solution which is not representative of a real process operation [b]. Several authors
87 developed different experimental methods to determine the IEMs resistance which includes
88 the use of direct polarization methods or impedance spectroscopy [c]. The membrane
89 resistance strongly depends on the concentration and composition of the electrolytic
90 solutions in contact with the membrane because it determines the water uptake and ionic
91 concentration profile in the membrane (i.e. Donnan equilibrium). The presence of
92 concentrated multispecies electrolytes promotes an increase in the resistance of the IEMs
93 which is explained by the lower activity of the ions present in the membrane with respect the
94 ions present in the bulk electrolytic solution [d]. As a consequence, the lower ions activity in
95 the membrane promotes the lowering of water fraction in the membrane (i.e. membrane
96 shrinking) which induce a consequent constrict of hydrophilic channels for the ions transport
97 [e]. As reported in some studies, cation exchange membranes (CEM) resistance generally
98 resulted higher with respect anion exchange membranes (AEM) due to the difference in ion
99 mobility, which indicates the dependence of the IEMs resistance by the ionic species
100 concentration in the electrolytes [f]. Indeed, more detailed investigations clarified the reason
101 of the higher resistance in the CEM thank to the determination of the transported species
102 under cationic and anionic transport [g]. Being the OH⁻ species the most commonly
103 transported charge through the AEM, a lower gradient between membrane and bulk
104 solutions was obtained determining a lower resistance of the AEM membrane. On the
105 contrary, in the CEM membrane most of the ionic charge was transported by other species
106 than protons, which promote an increase of membrane solution concentration gradient and
107 ionic resistance[h]. In cases where Ohmic overpotentials have been characterized in BESs,

108 their value was often < 10% of the total overpotentials, while potential losses associated to
109 the pH split were much larger [ac].” A good example of permselectivity regulation is offered
110 by the work conducted on chloroalkali process in which several studies focused their
111 attention to the control and reduction of the OH⁻ transport through the CEM during the
112 chloroalkali process by the presence of the perfluorosulphonic polymer providing a good
113 OH⁻ blocking capacity [24]

114 As already mentioned, the use of IEMs, which transport cations and anions other than
115 protons and hydroxyls, results in the pH splitting between the anodic and cathodic
116 compartments of a BESs due to the ion transfer through the electrolyte and the IEM [25].

117 When looked in detail, the pH split between anode and cathode involves both CEM and
118 AEM separators, and it is mainly related to the higher concentration of other ionic species,
119 which compete with protons and hydroxyl ions [26, 27]. As reported in Fig.1, the migration
120 of ionic species being different from protons and hydroxyls at neutral pH is more favorable due
121 to their higher concentrations, mostly of the charged species is transported by species which do not
122 participate in the oxidation and reduction reactions. The continuous production of protons in
123 the anode and its simultaneous consumption by the reduction reaction at the cathode
124 generates an accumulation of protons in the anolyte (acidification) and an accumulation of
125 hydroxyl ions at the cathode (alkalization) coming from water autoprotolysis.



126

127 **Figure 1. Ionic transport and correlated pH split with the use of a cation (A) and an**
 128 **anion (B) exchange membrane.**

129 Alkali and acid production through the transport of ionic species is influenced by several
 130 parameters such as electrolytes composition, membrane permselectivity and current
 131 density. Even if similar modelling approaches for bioelectrochemical systems [I, II], which
 132 involved the use of the mass and electron balances along with the equations that describes
 133 the ion transport through an ion exchange membrane, have been described in the literature,
 134 a comprehensive model which describes the pH split phenomenon has not yet described.
 135 The most recent models adopted the assumption of an infinite fast acid-base reactions which
 136 makes numerical analysis much easier [III]. By the infinite fast rate assumption, already
 137 described in the literature, all the fluxes of the ions and the pH profile during the
 138 bioelectrochemical cell operation have been described [IV].

139

140 While anions and cations are transported across the selective IEMs or blocked as counter
141 ion (depending on the type of IEMs adopted), even uncharged molecules can also be
142 transported by diffusional phenomena through the IEMs. Uncharged species being
143 transported only by diffusional forces, while the uncharged molecules are not influenced by
144 the electric field and the fixed charge groups present on the ion exchange membrane
145 surface. However, even if the diffusion of uncharged molecules is not correlated to the
146 electrons flow in the bioelectrochemical device, the diffusion of uncharged molecules can
147 influence the bioelectrochemical reactions coulombic efficiency. As reported in the literature,
148 the diffusion of organic substrates from a COD oxidizing bioanode to a methanogenic
149 biocathode improved methane generation by the activation of acetolactic pathways, which
150 did not include electroactive microorganisms leading to an overestimation of the efficiency
151 of the bioelectrochemical reaction [i]. The acidification of the anodic chamber and the
152 alkalization of the cathodic one promotes two main disadvantages for the process operation;
153 the first one is linked to the biofilm stability, while the energy loss due to the pH gradient
154 decreases the power output or the power consumption of a bioelectrochemical process for
155 the microbial fuel cell (MFC) and microbial electrolysis cell (MEC), respectively [28]. The
156 anodic oxidation reaction releases protons, which provoke a local acidification near the
157 anodic surface; this local acidification decrease severely affects the microorganisms'
158 activity, limiting the electrocatalytic activity of the biofilms [29, 30]. The cathode reduction
159 reaction consumes protons (or releases hydroxides), causing the alkalization of the
160 chamber. Alkalization also decreases the microorganisms' activity, promoting a partial or
161 complete inhibition of the biofilm [31]. Moreover, other possible effects related to the pH
162 increase are the precipitation of cations like Ca^{2+} or Mg^{2+} on the surface of cathode, which
163 promotes the surface fouling of the cathodic material [32-35]. The fouling of the cathodic
164 material is particularly disadvantageous in benthic MFCs because of the increased

165 concentrations of earth alkaline cation species in seawater [36]. In terms of electrochemical
166 losses, the pH split between anode and cathode promotes the creation of an additional
167 overpotential related to the different proton concentrations; the pH gradient develops over
168 the membrane, causing further potential drop of about 59 mV for each unit of pH [37].

169 The ion migration through the electrolytes and the IEM depends on the reaction rates of the
170 bioelectrochemical reactions, which is described by the current density; an increase in the
171 current density is linked to the acidity and alkalinity generation in the two compartments of
172 a BESs. The consequent pH split is an undesirable condition of the MFC that negatively
173 affects the energy output and the long-term stability of the process. In order to mitigate the
174 pH split in the MFC devices, several researchers proposed the utilization of different
175 separators including IEMs, porous membrane and bio-separators along with the
176 maintenance of the separation of the electrolytes between the anodic and the cathodic
177 compartments. Alternatively, researchers have proposed the addition of an acid on the
178 cathode, such as CO₂, to mitigate the pH gradient and associated potential loss [38].

179 Differently, the energy losses in a MEC due to the ionic transport and the pH split introduce
180 an additional energy consumption of the system, which is generally a disadvantageous
181 effect [39]. However, with a new conceptual view, the pH split in a MEC results in an
182 advantageous phenomenon that can be used for several environmental applications. This
183 review summarizes the different bioelectrochemical applications in which pH split
184 phenomenon and the associated effects are exploited for environmental applications
185 including the recovery of CO₂ electrosynthesis products, the nutrient recovery, the biogas
186 upgrading, the water desalination/softening and the removal of recalcitrant pollutants. In this
187 frame, the pH split phenomenon can be exploited to control the bioelectrochemical process
188 used for several environmental applications, thanks to the possibility of continuously
189 generating acidity or alkalinity in different compartments. A MEC can be considered as an
190 interesting tool, in which the concept of a secondary microbial electrochemical technology

191 (MET) can be realized [40], optimizing the utilization of the electrical energy both for products
192 generation/treatment and for their extraction and refining.

193
194 **2.1. Products extraction and recovery in bioelectrosynthesis**

195 Bioelectrochemical reduction of CO₂ is an attractive strategy to combine renewable electrical
196 energy storage and CO₂ conversion into valuable products from industrial exhaust [41, 42].
197 The interest of industrial users and governments for the combination of energy storage and
198 CO₂ emission mitigation promoted several actions toward the scale up of the
199 bioelectrochemical CO₂ reduction into fuels and chemicals, starting from industrial off-gases
200 and CO₂-rich streams [43, 44]. **Electrochemical CO₂ reduction into valuable products**
201 **represent a promising strategy to couple CO₂ emission mitigation and excess renewable**
202 **energy storage into storable fuels. Besides Sabatier reaction which constituted the principle**
203 **of the power to gas approach [l], the application of external voltage across catalytic**
204 **electrodes allowed the production of several products including solid carbon, hydrocarbon,**
205 **and oxygenated species [m]. Depending on operating conditions adopted which includes**
206 **temperature, ion transport medium, electrochemical cell configurations and catalytic**
207 **materials, the electrochemical CO₂ reduction permit to transform the stable CO₂ molecules**
208 **into C1-C4 chemical compounds available for further chemical exploitation [n]. The use of**
209 **BESs for CO₂ reduction, also named bioelectrosynthesis presents some potential**
210 **advantages compared to electrochemical CO₂ reduction processes, including the lower**
211 **energy low energy input required to activate the CO₂ reduction, the use of mild operating**
212 **conditions in (i.e. temperature and pressure) the capacity of self-regeneration of the**
213 **microorganisms and the high selectivity with minimal side reactions for the target products**
214 **[o]. Usually, electrochemical CO₂ reduction processes offers higher coulombic efficiencies**
215 **for the target products [p], in the range of 92-99 % of selectivity on the other hand,**

216 bioelectrochemical approaches requires lower energy inputs and more easily process
217 operation and control [q]

218 The microbial electrosynthesis (MES) is defined as the utilization of microorganisms in the
219 cathodic chamber of a BESs to produce organic molecules from a CO₂ stream, wherein the
220 electroactive microorganisms are responsible for the electrons transfer and production of
221 chemicals [45-47]. The long-term stability of MES processes and the smart conversion of
222 electricity into CO₂ reduction to products shows good perspectives for the scale up of this
223 technology in the frame of circular economy and added-value products generation [48-50].
224 Even if several authors reported the possibility to obtain the CO₂ conversion into acetate
225 and other products by pure cultures or mixed microbial consortia [51-54], one of the main
226 bottleneck of the electrosynthesis process is the low product concentration obtained by a
227 simple production approach [55]. The higher acetate production rates reached 3.1 g/L d [56].

228 Products extraction separation and enrichment results in a major limitation of several
229 biotechnological processes, i.e. it has been estimated that more than 60% of the production
230 costs of the plant should be invested to separate and recover the final products (Bechtold
231 ett al 2008). Low cost and efficient separation technologies are highly required in
232 biotechnology industry an interesting approach to overcome the extraction ad purification
233 issue is offered by the “In situ product recovery” (ISPR) which consists in the integration of
234 the production and the separation in the same reactor [r]. Selective membranes are optimal
235 candidate to accomplish the ISPR objectives [s], i.e. several examples of integrated
236 production and extraction approaches have been reported in the literature by the adoption
237 of submerged membranes or in an external configuration creating an external loop process
238 [t,u]. Among membrane processes, the use of ionic exchange membranes in electrodialysis
239 processes constituted an attractive approach being a fast treatment which provides the
240 effective removal of uncharged molecules allowing the simultaneous concentration of the
241 target product [v]. Several electrodialysis applications have been proposed in the literature

242 for the in-situ lactate recovery to increase lactate concentration and reduce its inhibition
243 effect of the fermentation broth [z]. Similarly, the utilization of selective IEMs in in
244 bioelectrosynthesis processes results an attractive application of the ISPR concept to the
245 CO₂ fixation into VFAs.

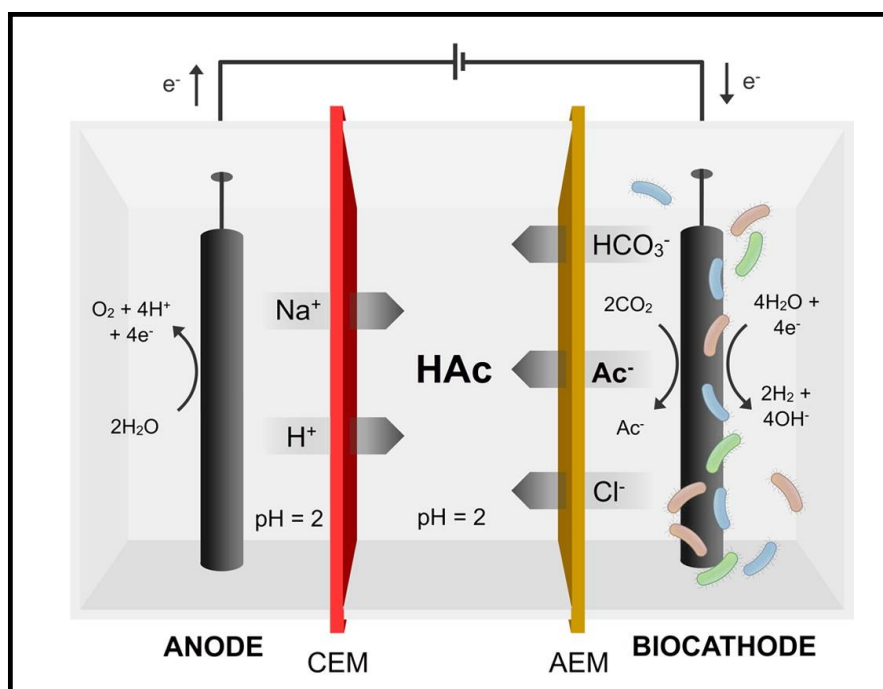
246 The advantage of the utilization of an electro-microbial technology is offered by the use of
247 the electrical current to supply the reducing power and the target migration of species due
248 to the electroneutrality maintenance. In the specific case of the production of a carboxylate,
249 the use of an AEM promotes the migration of the target products, which in turn can be easily
250 protonated by an acid environment, preventing undesired retro diffusion of the products due
251 to the concentration gradients [57, 58].

252 A first arrangement which exploited the pH split phenomenon to the acetate extraction via
253 membrane electrolysis, has been proposed by adopting a conventional two chamber MEC
254 equipped with an AEM, which promotes the migration of the acetate produced in the cathode
255 through the abiotic anode [57]. The acetate and the other carboxylates are protonated and
256 recovered as volatile fatty acids (VFAs) in a clean acidic anolyte due to the acidity production
257 promoted by the pH split. Moreover, the acetate concentrated at an average concentration
258 of 14 g/L was converted to ethyl acetate by the addition of ethanol in a separate unit heated
259 at 70 °C. The integrate bioelectrochemical process allowed for the production of 2.64 g/Lh
260 to ethyl acetate, with a final total conversion of 58 ± 3%.

261 The integration of CO₂ reduction into acetate and its in-situ extraction by the electromotive
262 force, has been also analyzed and modeled by Matemadombo and coworkers, in their
263 work, two different microbial electrosynthesis cells equipped with an AEM membrane were
264 utilized for the elaboration and the validation of a mathematical model that described the
265 simultaneous acetate production and separation from the cathode chamber to the anode
266 chamber. Despite the low acetate titate obtained in the two microbial electrosynthesis cells,
267 the 24% and 18% of the produced acetate migrated from the cathode to the anode

268 compartments reaching a concentration of 240 mg/L. Based on the mathematical model
269 assumptions, being the flux of acetate from the cathode to the anode proportional to the
270 applied electric potential, acetate migration can be enhanced by increasing the applied
271 potential to the cell [ad].

272 Furthermore, with a similar approach, a three-chamber MEC to boost the extraction
273 efficiency of the acetate and the other products [58]. The three chamber MEC (Fig. 2-A) was
274 constituted by a biological acetogenic cathode separated by an AEM from a saline extraction
275 compartment, which was separated from the anodic compartment by a CEM to exclude
276 possible chlorination of the acetic acid. By using a galvanostat, the CO₂ has been converted
277 into organic carbon via homoacetogenesis and products have been extracted in the
278 intermediate chamber of the reactor configuration.



279

280 **Figure 2. Three chamber microbial electrolysis cell for the acetate production and**
281 **extraction [58] (A) Reproduced with the permission of American Chemical Society**
282 **(ACS).**

283

284 During the operation of the three chamber MEC, an average pH of 8.4 was measured in the
285 catholyte, while in the extraction and in the anode compartment an average pH of 1.7 and 2

286 was determined, respectively. The three chamber MEC concept allows to reach an average
287 acetate production rate of 0.7 g/Ld, accounting for a coulombic efficiency of the cathodic
288 reaction of 76%, while in the first operational cycle an extraction rate of 22 g/m²d,
289 corresponding to a recovery efficiency of 99%, was obtained. The three chamber MEC
290 allowed to obtain an acetate solution with an average concentration of 13 g/L, showing the
291 concentration potential of the three chamber MEC controlled by the pH split phenomenon.
292 It is noteworthy to mention that as reported by the authors, during a failure in the CO₂ supply
293 into the cathodic chamber, the catholyte pH sharply increased to 11.6 due to lack of buffer
294 effect promoted by the CO₂ dissolution; this demonstrates the important effect of the pH split
295 phenomenon, which results by the adoption of almost neutral electrolytes. The three
296 chamber MEC concept has been further investigated and optimized with a modified three-
297 chamber MEC concept, in order to optimize the acetate production and extraction by the
298 energetic point of view [59]. As reported by the authors, the extraction efficiency obtained in
299 the previous work was low because of the acetate production rate, which accounted for the
300 5–8% of the charge balancing. Indeed, as 8 moles electrons are required per mole of acetic
301 acid produced, the protonation and the extraction of the monovalent acetate ion requires
302 one electron; this means that with a 100% coulombic efficiency, only 12.5% of the current
303 can be transported by the acetate anion. It was proposed to run the three chamber MEC by
304 imposing a current to ensure an almost complete coulombic efficiency; thus, an additional
305 reducing power was supplied to the cathodic acetogenic chamber as molecular hydrogen,
306 which was produced by a commercial electrolyzer. By this configuration, a considerable
307 increase in terms of acetate concentration was obtained, reaching 35 g/L of acetate in the
308 extraction chamber. Also, a strong acidic pH was maintained in the anodic and extraction
309 chamber thanks to the transport of different ions instead of protons and hydroxyls. Finally,
310 the study showed that a higher extraction capacity was obtained by supplying an external H₂
311 source, and indicated that the adoption of a three chamber MEC offers an interesting

312 approach for both the production and the extraction of a target compounds produced from
313 CO₂. Moreover, the adoption of three chamber MEC configuration can result in an increase
314 of the productivity, coupling the effect of the product removal with the in-situ pH control; the
315 base and acid dosages, which are usually adopted for the pH control of conventional
316 processes to prevent product inhibition and the product stream acidification, are fully
317 replaced by in situ production of hydroxyls (at the cathode) and protons (at the anode). The
318 electrochemical acetate production can be considered a secondary MET, in which the
319 reactor not only provides the reducing power necessary for the electrosynthesis but also
320 increases the process stability and the product extraction through the pH split.

321 A similar concept, with an innovative two cathode configuration was recently proposed by
322 researchers at AWMC (Australia) focused not only on the acetate production but also in C4-
323 C6 carboxylic acids. It was reported that, maintaining a slightly acidic pH in the cathodic
324 chamber of a biocathode can result in the solventogenesis, promoting the production of short
325 chain VFAs (e.g. butyrate and caproate) [60].

326 In this configuration, the pH control in the cathodic chamber was ensured by the CO₂ supply
327 (around the value of 5.4), which is necessary for the methanogenesis inhibition. A new
328 concept of three-chamber electrochemical system, consisting of two biocathodes and one
329 abiotic anodic chamber, has been adopted for the optimization of the acetogenic/chain
330 elongation and solventogenesis step in an integrated bioelectrochemical process [61]. In the
331 new dual cathode reactor, the acetogenesis and chain elongation are kept separated from
332 solventogenesis process and it allows to operate under optimal pH conditions without the
333 addition of chemicals and CO₂ gas sparging. During operation, while the cathode dedicated
334 to the acetogenesis/chain elongation reaction was maintained at pH of 6.9 through the direct
335 CO₂ sparging, in the solventogenesis, the cathodic pH is maintained around the value of 4.9
336 through the CO₂ bubbling from the biocathode and an alternating control of the
337 electrochemical potential of cathodes.

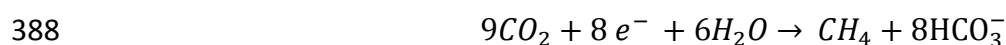
338

339 **2.2 Biogas upgrading through BESs**

340 The biogas upgrading process, which consists in the CO₂ removal from the biogas, is one
341 of the most attractive application of the bioelectromethanogenesis reaction that involves the
342 utilization of a biocathode aimed to the CO₂ reduction into CH₄. The biogas, produced during
343 **the anaerobic digestion (AD)** process, is typically composed of methane (CH₄) 40–75% and
344 carbon dioxide (CO₂) 15–60%. Through the biogas upgrading process, the biogas is
345 transformed into biomethane, with a CH₄ content of about 95%. The characteristics of the
346 biomethane are similar to those of the compressed natural gas and it may find applications
347 as a vehicle fuel or injected in the distribution grid [62, 63]. Among the different biogas
348 upgrading biobased solutions, which include in situ and ex situ strategies [64-66], an
349 innovative solution to reduce the power supply has been proposed which consists in the
350 CO₂ reduction into methane by the bioelectromethanogenesis (BM) reaction [67]. The BM
351 reaction consists in the use of methanogenic biocathode, in which the electrode supplies
352 the reducing power to the methanogenic biofilm growing on the electrode surface [68]. The
353 reducing power supply in the BM reactions can proceed by a direct, hydrogen-mediated or
354 hybrid mechanisms [69, 70]. Moreover, BM offers a new renewable energy storage concept
355 in which BM reaction allows to store the overproduction of renewable energy through the
356 methanization of the CO₂ contained in the biogas and other CO₂ rich streams. This
357 innovative concept has been named Bioelectrochemical Power to Gas [71].

358 The integration of the AD process and the BM reaction has been proposed as an in-situ
359 approach through the direct insertion of the electrodes into the AD tank; on the other hand,
360 in the ex situ approach, a methane-producing MEC can be used as a post-treatment unit for
361 the biogas treatment [72, 73]. The in-situ approach has been widely explored under
362 laboratory conditions; the reducing power supplied by the cathodic material permits to reach
363 higher methane concentration [74] in the produced biogas, while the oxidation at the anodic

364 compartment of the soluble COD increases the stability of the AD process with respect the
365 VFAs control [75]. However, the direct insertion of the electrodes in the AD digester can
366 affect the process stability as the CO₂ conversion into methane can promote the loss of
367 buffering power with a consequent inhibition of the methanogenic activity [76, 77].
368 Furthermore, the oxidation of the organic compounds performed by anodophilic bacteria
369 using the electrode as electron acceptor, required a lower energy input with respect to the
370 water oxidation reaction. Villano and co-workers, proposed the integration of a fully bio-
371 catalyzed methane producing MEC in cascade combined with an anaerobic digester; i.e.,
372 while the reduction of CO₂ biogas from an anaerobic digester occurred in the cathode, the
373 anodic oxidation of residual COD content in anaerobic digestate could partially sustain the
374 energy demand of the process; in this frame, the MEC post-treatment could enhance both
375 digestate and biogas quality [78]. Batlle-Villanova and co-workers recently proposed a
376 different integration of an AD with a methane producing MEC. The authors proposed to feed
377 the bio-cathode of a MEC with an effluent from a water scrubbing-like unit, where
378 hydrogenophilic methanogens convert the CO₂ into CH₄, instead of directly connecting the
379 MEC to the digester [79].
380 Xu and co-workers proposed the utilization of methane producing bio-cathode for the
381 reduction of the CO₂ contained in the biogas into additional methane, similar to previously
382 reported studies. Due to CO₂ dissolution in the cathodic chamber, the alkalinity generation
383 increased the upgrading performances [80]. Along with the BM reaction that is responsible
384 for CO₂ reduction into CH₄, the alkalization of the cathodic chamber results in an important
385 additional CO₂ removal mechanism. Considering the CO₂ reduction into CH₄, it is possible
386 to obtain a maximum removal of 9 moles of CO₂ for each mole of CH₄ generated at the
387 cathode according to the following equation [81]:

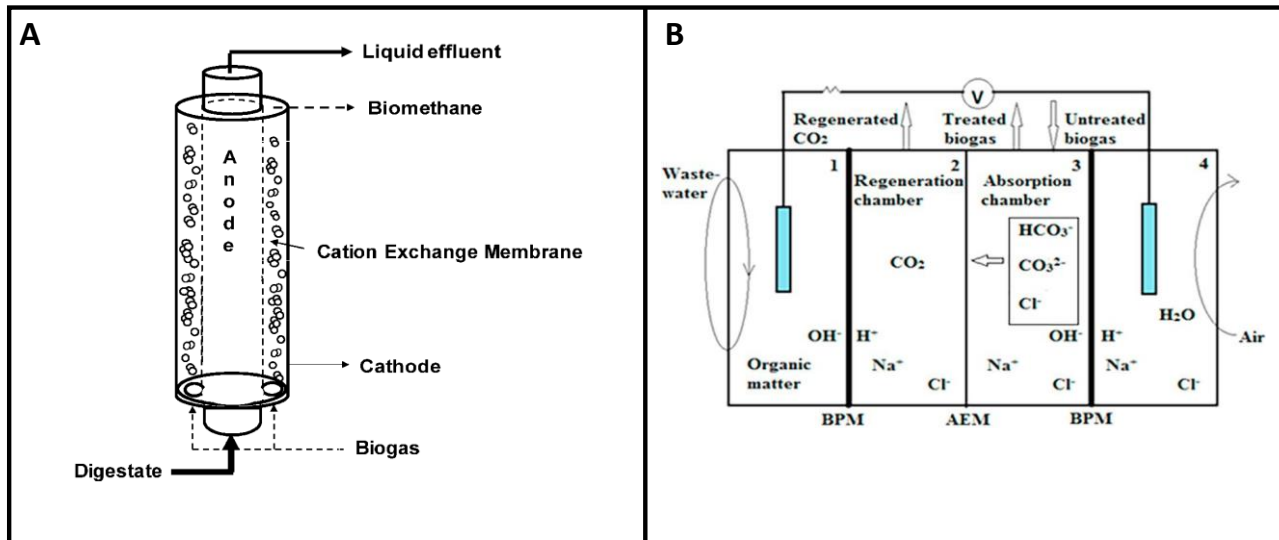


389 Another interesting integration of the BM reaction and an AD digester has been proposed in
390 literature, where a methane-producing MEC works as a post treatment unit of both digestate
391 and biogas [82, 83]. Through the integration of a bioanode and a biocathode, the residual
392 COD content in the digestate partially sustains the energy demand of the process, which is
393 mainly devoted to the CO₂ conversion into CH₄. Another aspect related with the integration
394 of a fully biological MEC and an AD process is the possibility to obtain the ammonium
395 migration and recovery. A three chamber MEC has been also presented as post-treatment
396 unit to refine digestate, to upgrade the biogas and to recover the nutrients like ammonium
397 [84]. In the proposed configuration, the cationic and anionic migration across the
398 membranes, permits the accumulation of ammonium bicarbonate in an intermediate
399 chamber; the three chamber configuration has been developed to combine the ammonium
400 removal from a liquid effluent and the CO₂ removal from a gas in a single device. The three
401 chamber concept has been further optimized by the set-up of two-side cathode
402 configuration, in which the two cathodic compartment, connected in parallel by a titanium
403 wire, maximize the volumetric area of the reactor devoted to the CO₂ removal through the
404 BM reaction and the cathodic alkalinity generation [85]. The two-side cathode promoted a
405 higher CO₂ removal while minimizing the energy consumption of the whole process. The
406 integration of the CO₂ removal for biogas upgrading has been investigated in a scaled-up
407 MEC with a tubular configuration (Fig. 3-A).

408 In this configuration, the outer biocathode performs the CO₂ removal thanks to the BM
409 reaction and the alkalinity generation; on the contrary, the energetic demand of the process
410 is partially sustained by the bioanode, which bioelectrochemically oxidize the organic matter.
411 A tubular reactor equipped by an AEM has been tested under both potentiostatic three
412 electrode configuration and by a two-electrode configuration polarization. Despite the good
413 CO₂ removal performances, the two-electrode polarization strategy resulted in a higher
414 energy consumption and a limited effect on the CO₂ removal mechanism [86]. Moreover, a

415 similar reactor configuration equipped with a CEM has been tested for the simultaneous
416 ammonium recovery and CO₂ removal (Fig. 3-A).

417



418

419 **Figure 3. Tubular MEC for simultaneous biogas upgrading and ammonium recovery**
420 **[87] (A). Reproduced from Open access licence from MDPI. The microbial separation**
421 **cell aimed to CO₂ removal for biogas upgrading [88] (B). Reproduced with the**
422 **permission of Elsevier.**

423

424 The CO₂ removed using this configuration was higher thanks to the possible migration of
425 Ca²⁺ and Mg²⁺, which introduced another CO₂ removal mechanism promoted by the
426 precipitation of insoluble carbonates [87]. The pH split phenomenon that takes place in the
427 anode and the cathode due to the ionic transport has been also exploited in a microbial
428 electrochemical separation cell (MESC), supplied with four compartments and anion and
429 bipolar ion exchange membranes. In this configuration (Fig. 3-B), the pH increase of the
430 adsorption chamber led to the CO₂ sorption into HCO₃⁻, while the pH decrease of the
431 regeneration chamber resulted into the release of CO₂ [88].

432

433

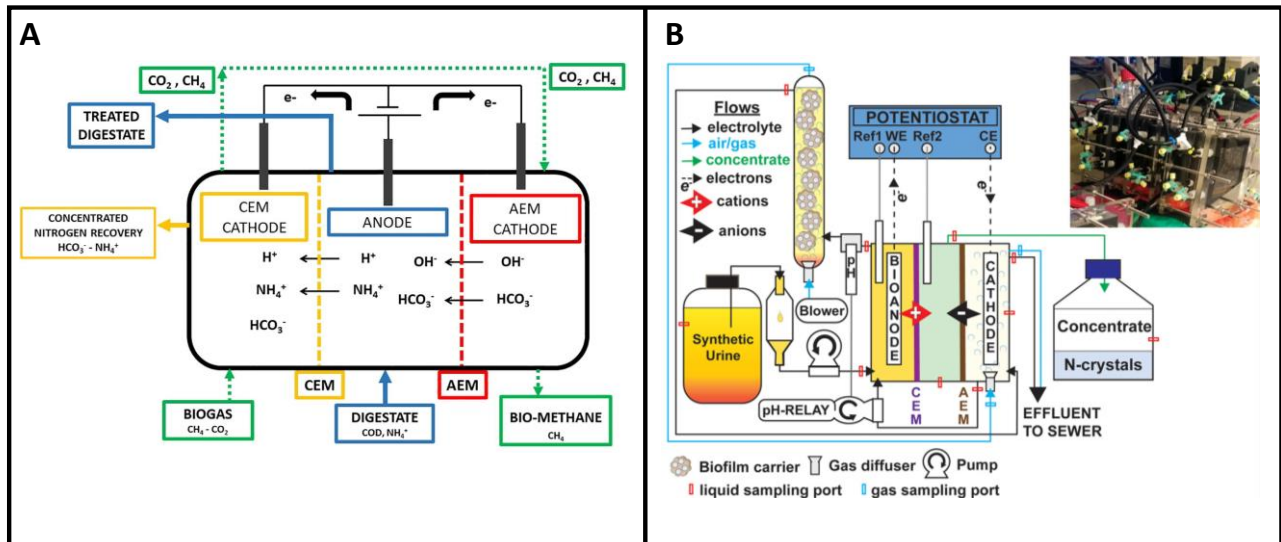
434 2.3 Nutrients recovery: nitrogen recovery through BESs

435 The use of synthetic fertilizers strongly impacts the human way of life on the planet while
436 the benefits on the agricultural production results in a generic increase in the quality of life
437 of the human population. However, the increase of the population promotes some
438 environmental issues related to the use of unsustainable model of development. The main
439 elements necessary as nutrients are the nitrogen (under ammonia form) and the
440 phosphorous (under phosphate or orthophosphate form). While ammonia is produced
441 through the Haber Bosh process, phosphorus is extracted by mining different minerals.
442 Haber Bosh is an energy intensive process (2% of the worldwide energy) in which the
443 atmospheric nitrogen is converted into ammonia by the use of hydrogen and Fe-Ni catalysts,
444 under high pressure and temperature conditions [89]. At the end of its life cycle, the
445 ammonium nitrogen contaminates the water due to the eutrophication action, in which the
446 unregulated growth of microorganisms promotes the progressive loss of the flora and fauna
447 of the environmental acceptor. Tertiary treatment in wastewater treatment plant is devoted
448 to the ammonium nitrogen conversion into molecular nitrogen through the nitrification
449 denitrification process [90].

450 The ammonium migration and diffusion across a PEM/CEM phenomena has been reported
451 by several authors. Viridis and co-workers demonstrated that both migration and diffusion,
452 permits the accumulation of ammonium nitrogen in the cathodic chamber [91]. **As mentioned**
453 **above**, in neutral electrolytes involved in bioelectrochemical process (e.g. wastewater), the
454 higher concentrations of ammonium result in a much more favourable migration of
455 ammonium and other cations compared to the protons transportation to maintain the
456 electroneutrality of the system. Cord-Ruwisch demonstrated the exploitation of the
457 ammonium/ammonia as as a proton shuttle, accounting for the 90% of ionic flux in the
458 system, in a two chamber MFC to prevent anolyte acidification [92]. The use of an MFC or
459 a MEC for the ammonium removal/recovery changes the perspectives in terms of energy
460 consumption, i.e. in the MFC a negative energy process allows to the recovery of ammonium

461 but its performances are negatively influenced by the presence of a strong pH gradient
462 between the anodic and cathodic chamber. On the other hand, even if the use of a MEC
463 requires an energy input, the ammonium recovery rates can be increased by several times
464 resulting in a more efficient strategy for the ammonium recovery and reutilization as a
465 concentrated product [93]. Ammonium migration was also documented in other BESs such
466 as MECs and microbial desalination cells (MDCs) [94, 95]. In a continuous flow MEC aimed
467 at the production of methane, the ammonia migration through a Nafion117 membrane allows
468 for the concentration of ammonium 10 times higher than the influent concentration [78]. By
469 feeding the same MEC with a real effluent coming from the dark fermentation step of a two-
470 stage AD process rich in ammonium, the ammonium migration increases its contribution to
471 the overall electroneutrality maintenance from 2 to 20% [96]. The utilization of MEC for the
472 water desalination has been called MDC, in which the current generated or consumed by
473 electroactive microorganisms promotes the transfer of ionic species out of water [97].
474 The MDC are composed by three or more chambers separated by different ion exchange
475 membranes, similar to the conventional electrodialysis devices [98]. As previously reported
476 for the CO₂ removal aimed at biogas upgrading, an integrated three chamber MEC has been
477 successfully operated; the CO₂ removal has been coupled with the ammonium recovery,
478 exploiting the current generated by a bioanode. The utilization of a conventional
479 accumulation chamber showed a recovery of an ammonium bicarbonate concentrated
480 solution [84]; in particular, the ammonium migrated from the anodic to the accumulation
481 chamber through a PEM while the CO₂ (from a synthetic biogas adsorbed in the cathode
482 under the HCO₃⁻ form) migrated from the cathodic to the accumulation chamber due to the
483 presence of the AEM. The use of an AEM with a low selectivity allowed the ammonium
484 diffusion from the accumulation to the cathode compartment. The successful recovery of the
485 ammonium ion in one chamber has been overcome by the adoption of a two-side cathode

486 configuration (Fig. 4-A), which allowed the integration of CO₂ removal with the ammonium
 487 recovery by the bioelectrochemical COD oxidation at lower energy consumption [85].
 488



489
 490 **Figure 4. Two side cathode MEC configuration for simultaneous ammonium recovery and biogas upgrading [85] (A). Reproduced with the permission of Elsevier. Three**
 491 **chamber MEC operated for the ammonium recovery from source separated urine [99]**
 492 **(B).**
 493

494
 495 Recently, a first attempt of an integrated fully biological MEC used as a post treatment unit
 496 of AD process showed the important role of the ammonium migration in a scaled up tubular
 497 reactor [87]. The tubular reactor, equipped with a CEM, has been operated under three
 498 different ammonium loads applied to the anodic compartment. This study highlights the
 499 effect of the ammonium load on the reactor performances and describes the increase of the
 500 ammonium migration to the cathode chamber as a function of the applied anodic ammonium
 501 load, which increased from 1 to 100% of the transported charge.

502 Moreover, by the adoption of an MDC type reactor, the ammonium ions can be transferred
 503 from the middle to the aerobic cathode compartment for the nitrification step [100]. The
 504 possibility to reach the complete ammonium recovery in a BES has been obtained by
 505 combining the alkalinity generation in the cathodic chamber with a stripping process. By

506 using this approach, the ammonia recovery was obtained through catholyte aeration and
507 subsequently ammonia adsorption in an acid solution of a MFC [101]. In addition, the
508 ammonia recovery by catholyte stripping has been investigated as a strategy to mitigate the
509 ammonium inhibition of the AD process, in which the use of a MFC resulted in ammonia
510 removal efficiency of 100% [102]. It has been demonstrated that higher current densities
511 can be exploited to increase the ammonia recovery in an MFC, obtaining a 61% of
512 ammonium transported by electricity-driven migration [103]. The alkaline pH characterizing
513 the cathodic compartment, drives the ammonium to ammonia gas. An application of this
514 interesting aspect has been reported in a study conducted by Wu and Modin, where the
515 recovery of ammonia has been combined with hydrogen production in a MEC treating reject
516 waters [95]. These waters are characterized by high concentration of ammonium (around 1
517 g/L) but low concentrations of organic compounds. Due to the current generation, a pH
518 increase up to 12 has been detected in the cathodic compartment of the cell, resulting in an
519 ammonia recovery of 96% in the synthetic reject water and 79% in the real reject water. The
520 alkalisation of the catholyte has been also tested in single chamber MEC for the
521 precipitation of struvite; even if no ion exchange membranes are present in a single chamber
522 configuration, it has been demonstrated that local alkalisation in the area near the cathodic
523 surface is interesting for the struvite precipitation caused by a local pH increase [104]. The
524 ammonium recovery by ammonia stripping can be adopted as a strategy to increase the
525 recovery efficiency from wastewaters. The ammonium recovery has been deeply
526 investigated in several MDC devices devoted to the recovery of ammonium from urine;
527 several international research actions have been focused on the development of a combined
528 bioelectrochemical process aimed at simultaneously treating the source separated urine and
529 recover not only the ammonium but also elements to reuse as a fertilizer [105, 106]. In the
530 several solutions proposed, the organic load of the urine has been used to generate the
531 electrons driving the ammonium migration. It is noteworthy to observe that the development

532 chain of the bioelectrochemical technology started from a simple MFC, i.e. urine has been
533 proposed as convenient feed-stream for producing electricity in MFCs [107]. A first MFC
534 using urine as feeding solution resulted in a maximum power output of 0.25 W/m², while a
535 9.6 gN/m²d were recovered by ammonium migration [101]. Ammonium has been recovered
536 from urine through a MEC tested along with the hydrogen production, showing a recovery
537 rate of 162±10 g/m²d with a columbic efficiency of 84 ±1% [108]. A MDC cell was operated
538 with a synthetic urine to recover ammonium nitrogen and potassium from urine (Fig. 4-B).
539 The MDC reached a current density of 50 A/m² by controlling the anodic chamber 0.2 V vs
540 SHE, which promoted the removal and the recovery of nitrogen, phosphorous and
541 potassium (average rates of 7.18 kgN/m³d, 0.52 kgP/m³d and 1.62 kgK/m³d, respectively).
542 Moreover, the study reports the possibility to obtain a nitrogen-rich solid in the form of pure
543 NH₄HCO₃ crystals containing 17% of nitrogen by flash-cooling of the obtained concentrate
544 at 4 °C [99]. Another approach has been proposed to electrochemically remove and recover
545 ammonia, exploiting the cathodic alkalinity generated by an electric field, which promoted
546 the ammonium ions migration towards the wastewater-air interface. The ammonia removal
547 and recovery are based on the electrochemical oxidation, and the electrochemically assisted
548 surface transfer mechanism. The ammonia was recovered thanks to the floating electrode
549 approach, without the presence of IEMs [109].

550

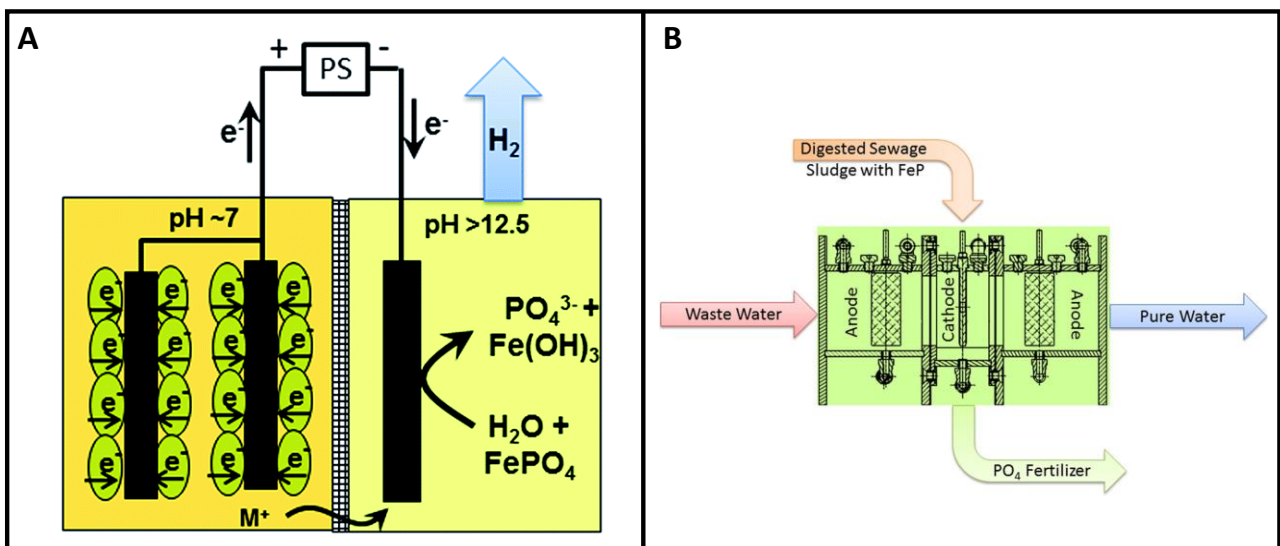
551 **2.4 Phosphorous recovery/remobilization**

552 Phosphorus is an essential element which is mined all over the world and, in particular, on
553 a large scale in the USA, China and Morocco [110]. Phosphorous is a component in
554 synthetic fertilizers and its demand is increasing at 3–4% per year [111]. Phosphorus also
555 represents an important inorganic nutrient and pollutant, mainly recovered by chemical
556 precipitation or biological processes during tertiary treatment in the wastewater treatment
557 plant [112]. For the recovery of the phosphorous, as previous reported for the ammonium,

558 several studies were conducted on the possibility to use a MFC to obtain the struvite
559 ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation on the cathodic surface of single-chamber devices [113].
560 This approach permits to stimulate the struvite precipitation thanks to the local alkalisation
561 that occurs close to the cathodic surface of the cell; even if in a single chamber cell the
562 anolyte and the catholyte are constituted by the same media, mass transfer limitations
563 occurs due to the presence of other ions at significantly higher concentrations, which are
564 responsible for the electroneutrality maintenance [114]. Cusick and Logan demonstrated the
565 possibility of removing up to 40% of soluble phosphate by struvite precipitation (0.3– 0.9
566 $\text{g/m}^2 \text{ h}$) using a single chamber MFC approach [115]. The single chamber MFC was tested
567 for the recovery of struvite from real waste streams such as swine manure [116] and urine
568 [117]. The MFC removed up to 94% of the soluble phosphorus present in the urine due to
569 the excess of ammonium, while by testing the swine manure a soluble phosphorous removal
570 efficiency of 80% has been determined. Another approach used for the phosphorous
571 recovery by struvite crystallization has been proposed, which includes the use of a two
572 chamber MFC where the bioelectrochemical anodic reaction produces the necessary
573 equivalents for the reduction of the FePO_4 present in a digested sludge; this approach has
574 been used to remobilize insoluble phosphate into a soluble form available for the struvite
575 precipitation by dosing magnesium and ammonia [114]. Further, the remobilization of the
576 insoluble FePO_4 salt, which constitutes the by-product of the phosphate removal in the
577 wastewater treatment plant, is driven by the quantitative reduction of the Fe to Fe^{3+} ,
578 promoting the PO_4 remobilisation in the liquid phase. During the two-chamber operation, the
579 pH increased up to 9 in the abiotic cathode thanks to the use of the protons in the cathodic
580 reactions (i.e. iron and oxygen reduction); this promoted the production of the base that
581 remained in the catholyte, as alkali cations (M^{n+}), instead of protons migrated into the
582 cathode. The consequent alkalisation resulted in an additional phosphorous remobilization
583 due to the slightly alkaline pH. The MFC concept was shifted to a MEC concept (Fig. 5-A)

584 through the application of an external potential to increase the alkalinity production and the
 585 phosphorous remobilization from sewage sludge [118]. This study showed how the
 586 alkalisation of the cathodic chamber of a MEC, sustained by the anodic COD oxidation,
 587 can be successfully adopted as a strategy for the phosphorous remobilization thanks to the
 588 stimulation of a new mechanisms that involves a strong alkaline pH.

589



590

591 **Figure 5. Phosphorous remobilization through a microbial electrolysis cell [114](A).**
 592 **Reproduced with the permission of Royal Society of Chemistry (Great Britain).**
 593 **Scaled-up bioelectrochemical process for Phosphorous remobilization [119](B).**
 594 **Reproduced with the permission of Elsevier.**

595

596 By applying voltages between 0.2 and 6.0 V, a strong chemical base is generated thanks to
 597 the partial exploitation of the chemical energy contained in the anodic substrates. The study
 598 conducted by the use of a MEC resulted in a significantly faster phosphate remobilisation
 599 from iron phosphate with respect to the use of a MFC. Indeed, the use of a MFC involves
 600 the electrochemical reduction of the $FePO_4$ and an oxygen reduction mechanism that
 601 generates the alkalinity, while by using a MEC, the strong alkalisation of the catholyte
 602 favours a substitution mechanism, in which the phosphate is remobilized and $Fe(OH)_n$ is
 603 precipitated. Moreover, the second remobilization mechanism offered an additional

604 advantage in the case of the presence of heavy metals in soluble form that are precipitated
605 as insoluble hydroxides. A scaled-up reactor (Fig. 5-B), operated both under MFC and MEC
606 conditions [119], further confirmed the increase of the phosphate remobilization through the
607 application of an additional voltage due to the pH rise in the cathodic chamber. The study
608 performed the kinetic analysis of the fluid particle: while in the MFC configuration the
609 remobilization was performed by the diffusion in the liquid film around the sewage sludge
610 particle, in the MEC the reaction resistance moved inside the sewage sludge particle.

611

612 **2.5 Water sanitation and softening: alkali production, sulphide control and H₂O₂** 613 **disinfection**

614 As previously discussed, the increased pH in the cathode chamber of a BES can be used
615 to efficiently harvest an alkaline solution. Caustic soda is an extensively utilized chemical in
616 many applications such in the pulp and paper industry but also in the breweries and dairy
617 plants, where it is mainly used for cleaning process equipment. This generates wastewaters
618 with a high organic load that can be used to feed the anodic compartment of a BES. Indeed,
619 the consumption of the protons can be coupled with the transport of sodium and/or
620 potassium into the cathodic compartment; this produces a caustic solution, which comprises
621 sodium and/or potassium hydroxides. If a small clean water stream is introduced as the
622 influent cathode, the caustic solution can be harvested.

623 Rabaey and co-workers investigated the possibility of producing caustic during wastewater
624 treatment using a three-electrode configuration and operating in electrolysis mode. The
625 BES, equipped with a lamellar configuration, was operating at 1.77 V (1015 Am⁻³ volume of
626 the anodic chamber) to supply high amounts of electron donor from acetate [120]. In these
627 conditions, about 1.05 A was generated by the system, and up to 3.4 wt% caustic production
628 has been reached, at an acetate to caustic efficiency of 61%. Subsequently, a direct effluent

629 from a brewery process **was used** and currents of up to 0.38 A within a six-week operational
630 period **were obtained**.

631 Another application of BES could be represented by the water softening, which consists in
632 the calcium and magnesium removal from waters [121]. Hard waters have a damaging effect
633 on water infrastructures, which are usually treated through polymeric ion exchange resins.
634 As reported by Perumalsamy, a MDC concept could be applied for the remove of Ca^{2+} and
635 Mg^{2+} ions from water by their migration [122].

636 A three chamber MDC set up with an anode, a cathode and an intermediate salt
637 compartment, has been tested to remove hardness from several different hard waters, (220
638 to 2080 mg/L of CaCO_3). About the 90% of the hardness from the water samples has been
639 removed by a MDC exploiting of the electrons produced by a bioanode. Moreover, the MDC
640 removed 89% of the arsenic, 97% of the copper, 99% of the mercury, and 95% of the nickel
641 present in a synthetic solution [123]. Another study, where the bioelectrochemical generation
642 of electricity is not directly involved, reported an average calcium and magnesium removal
643 efficiency of 73–78% and 40–44%, respectively, reached at 5.8–7.5 $\text{kWh kg}^{-1} \text{CaCO}_3$ (0.77–
644 0.88 kWh m^{-3} water) [124].

645 The presence of hydrogen sulphide generated by sulphate reducing bacteria represents a
646 well know issue in sewer pipes [125, 126], which so far has been faced through the adoption
647 of conventional sulphide abatement strategies (e.g. preventing the formation of hydrogen
648 sulphide through the adoption of chemicals or mitigating the effect of generated hydrogen
649 sulphide). Recently, Lin and co-workers a strategy to electrochemically control the
650 production of sulphide in sewage has been proposed which consists in an in-situ oxidation
651 of iron combined to the generation of hydroxyl anions, using a single chamber membrane-
652 free system [127].

653 Even if in this study the role of the microorganisms supporting the electricity generation has
654 not been considered, the catholyte alkalinity generation resulted in an interesting application.

655 The sulphide was removed with an efficiency of $95.4 \pm 4.4\%$, reached applying a low voltage.
656 This setup successfully increased the sewage pH, avoiding the disadvantages linked to the
657 standard iron salt dosing and the use of chemicals for the sulphide precipitation. Moreover,
658 considering that higher pH shifted the equilibrium from volatile sulphide to non-volatile
659 sulphide, lower residual sulphide emission to the sewer atmosphere can be obtained [128].
660 Hydrogen peroxide (H_2O_2) is a chemical compound characterized by a strong oxidation
661 power exploited in several industrial applications (pulp and paper bleaching, synthesis of
662 chemical, and textile bleaching). Generally, the H_2O_2 is produced through anthraquinone
663 oxidation process or electrochemically approaches, which require significant energy inputs
664 [129, 130]. An alternative production method is represented by a MEC, where the oxidation
665 of wastewater organics at the anode is coupled to production of H_2O_2 at the cathode. For
666 this process, no expensive catalysts are needed as carbon materials have been already
667 tested for this reaction. An efficient production of H_2O_2 has been obtained in a MEC by
668 applying a voltage of 0.5 V; around 1.9 ± 0.2 kg $\text{H}_2\text{O}_2/\text{m}^3/\text{day}$ have been produced at
669 concentration of 0.13 ± 0.01 wt% and an overall efficiency of $83.1 \pm 4.8\%$. If a H_2O_2
670 concentration of 2–3 wt% can reached, the process can lead to several industrial
671 implications [131]. Even if the H_2O_2 production it is not linked to an alkaline pH, during the
672 experimental runs, the pH of the cathode increased from 7.2 ± 0.6 to 11.9 ± 0.5 after two
673 hours and it remained around 12 during the remainder of the experiments. The alkalization
674 of the catholyte resulted in an ion migration; the concomitant presence of a strong alkaline
675 pH represents a favourable condition for the advance oxidation of recalcitrant compounds.
676

Table 1. Different bioelectrochemical processes in which the pH split is exploited

Application	BES device	IEM	pH split utilization	Reference
Acetate extraction and concentration	MEC	AEM/BPM	Anode/extraction chamber acidification	[57, 58, 73]
Solventogenesis and acetogenesis control	MEC	AEM/CEM	Anode chamber acidification	[61]
CO ₂ removal - biogas upgrading	MEC	AEM/CEM/BPM	Cathodic alkalization	[80, 81, 88]
Ammonium recovery and concentration	MFC/MEC	CEM	Cathodic alkalization	[87, 101, 132, 133]
Ammonia stripping	MFC/MEC	CEM	Cathodic alkalization	[102, 103, 108]
Phosphorous recovery and remobilization	MFC/MEC	CEM	Cathodic alkalization	[114, 115, 118, 119]
Alkali production	MEC	CEM	Cathodic alkalization	[120]
Water softening	MEC	CEM	Cathodic alkalization	[98, 121, 123]
H ₂ S control in sewer	MEC	CEM	Cathodic alkalization	[127, 134]
Water sanitation	MEC	CEM	Cathodic alkalization	[131]

3. Perspectives of the pH split utilization in integrated bioelectrochemical processes

The pH split phenomenon takes place in the BESs because of the presence of physiological conditions which favour the microorganism's growth and activity. The pH split is an unfavourable phenomenon from a thermodynamic perspective, creating a potential gradient that decrease voltages in MFCs and increase applied voltages in MECs [26]. Despite this, the pH split offers new opportunities for several other bioelectrochemical applications. The acidification of the anodic chamber and the alkalization of the cathodic chamber promote a change in the physiochemical status of target species presents in the aqueous media. The pH split is directly linked to ionic species transport, which can be driven by the utilization of specific ion exchange membranes to control the migration of target species or to promote acidification and alkalization of the different compartments of a BES. In this new model concept, a bioelectrochemical device can be considered as an acidity-alkalinity production device, which enables the pH control without the necessity of strong acid and alkali dosing. Although real wastewaters present a limited buffer capacity which negatively affects process stability and performances in presence of pH split phenomenon, the pH control of anolyte and catholyte can be obtained by an appropriate selection of the operating conditions such as hydraulic retention time and current density, avoiding the use an external buffer which results in a not viable option to wastewater buffer capacity increase. Moreover, as recently determined in the literature, carbonate concentration largely impacts MFC anode performances [ab], suggesting the use of carbonate buffer instead of phosphate buffer in laboratory tests, being carbonate the most important buffer present in the real wastewater. This new concept allows for the integration of the effective bioelectrochemical process with other separation and purification steps, which usually represent the bottleneck of the application of several bio-based technologies. Throughout all the application described the utilization of a bioelectrochemical approach results in a more sustainable and cost-effective

solution, which still needs to be optimized in relation to the specific use and scenario of its applications. The most interesting future perspective offered by the present review work consists in the possible quantitative evaluation of the pH split phenomenon in a bioelectrochemical process. Indeed, an empirical or a mathematical model which correlates the amount of acidity/alkalinity in relation to media composition and current density would constitute an important scientific advance in the field of bioelectrochemical applications.

Conclusions

The pH split phenomenon in bioelectrochemical cells is caused by the use of neutral electrolytes that are necessary for the biological activity, along with the use of selective ionic membranes. For energy producing BES (i.e. microbial fuel cells), the pH split enables a power output decrease and a progressive loss of performances. On the contrary, in energy consuming BESs (i.e. microbial electrolysis cell), the pH split can be exploited to integrate the separation, concentration and recovery steps with the bioelectrochemical reactions. On the other hand, in an energy consuming BESs, the loss of efficiency introduced by the pH split can be reasonable sustained by a slightly higher energy consumption of the device. An advantageous perspective for pH split phenomenon exploitation in bioelectrochemical processes could be offered by the evaluation of a model in which the acidity/alkalinity generated in a BES, is expressed as a function of the current density and the composition of the electrolytes. On the other hand, an optimum between energy consumption and pH split phenomenon should be carefully considered for the process performances evaluation.

References

- [1] B.E. Logan, B. Hamelers, R. Rozendal, U. Schroder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Microbial fuel cells: methodology and technology, *Environmental science & technology* 40 (2006) 5181-5192.
- [2] B.E. Logan, K. Rabaey, Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies, *Science* 337 (2012) 686-690.
- [3] K. Rabaey, W. Verstraete, Microbial fuel cells: novel biotechnology for energy generation, *Trends in biotechnology* 23 (2005) 291-298.
- [4] L.T. Angenent, K. Karim, M.H. Al-Dahhan, B.A. Wrenn, R. Domiguez-Espinosa, Production of bioenergy and biochemicals from industrial and agricultural wastewater, *Trends in biotechnology* 22 (2004) 477-485.
- [5] M. Rosenbaum, F. Aulenta, M. Villano, L.T. Angenent, Cathodes as electron donors for microbial metabolism: Which extracellular electron transfer mechanisms are involved?, *Bioresource Technology* 102 (2011) 324-333.
- [6] F. Jiménez Otero, C.H. Chan, D.R. Bond, Identification of Different Putative Outer Membrane Electron Conduits Necessary for Fe(III) Citrate, Fe(III) Oxide, Mn(IV) Oxide, or Electrode Reduction by *Geobacter sulfurreducens*, *Journal of Bacteriology* 200 (2018) e00347-00318.
- [7] S.E. Yalcin, J.P. O'Brien, Y. Gu, K. Reiss, S.M. Yi, R. Jain, V. Srikanth, P.J. Dahl, W. Huynh, D. Vu, A. Acharya, S. Chaudhuri, T. Varga, V.S. Batista, N.S. Malvankar, Electric field stimulates production of highly conductive microbial OmcZ nanowires, *Nature Chemical Biology* 16 (2020) 1136-1142.
- [8] F. Wang, Y. Gu, J.P. O'Brien, S.M. Yi, S.E. Yalcin, V. Srikanth, C. Shen, D. Vu, N.L. Ing, A.I. Hochbaum, E.H. Egelman, N.S. Malvankar, Structure of Microbial Nanowires Reveals Stacked Hemes that Transport Electrons over Micrometers, *Cell* 177 (2019) 361-369.e310.

- [9] F. Aulenta, A. Catervi, M. Majone, S. Panero, P. Reale, S. Rossetti, Electron Transfer from a Solid-State Electrode Assisted by Methyl Viologen Sustains Efficient Microbial Reductive Dechlorination of TCE, *Environmental science & technology* 41 (2007) 2554-2559.
- [10] F. Aulenta, V.D. Maio, T. Ferri, M. Majone, The humic acid analogue antraquinone-2,6-disulfonate (AQDS) serves as an electron shuttle in the electricity-driven microbial dechlorination of trichloroethene to cis-dichloroethene, *Bioresource Technology* 101 (2010) 9728-9733.
- [11] H. von Canstein, J. Ogawa, S. Shimizu, J.R. Lloyd, Secretion of Flavins by *Shewanella* Species and Their Role in Extracellular Electron Transfer, *Applied and environmental microbiology* 74 (2008) 615-623.
- [12] A. Bard, J. Faulkner, *Electrochemical methods Fundamentals and Applications*, Wiley 2001.
- [13] O. Schaetzle, F. Barrière, K. Baronian, Bacteria and yeasts as catalysts in microbial fuel cells: electron transfer from micro-organisms to electrodes for green electricity, *Energy & Environmental Science* 1 (2008) 607-620.
- [14] X. Jiang, D. Chen, Y. Mu, D. Pant, H. Cheng, J. Shen, Electricity-stimulated anaerobic system (ESAS) for enhanced energy recovery and pollutant removal: a critical review, *Chemical Engineering Journal* (2021) 128548.
- [15] M. Zeppilli, M. Villano, F. Aulenta, S. Lampis, G. Vallini, M. Majone, Effect of the anode feeding composition on the performance of a continuous-flow methane-producing microbial electrolysis cell, *Environmental science and pollution research international* 22 (2015) 7349-7360.
- [16] R. Karthikeyan, A. Selvam, K.Y. Cheng, J.W.-C. Wong, Influence of ionic conductivity in bioelectricity production from saline domestic sewage sludge in microbial fuel cells, *Bioresource Technology* 200 (2016) 845-852.

- [17] E. Martinucci, F. Pizza, D. Perrino, A. Colombo, S.P.M. Trasatti, A. Lazzarini Barnabei, A. Liberale, P. Cristiani, Energy balance and microbial fuel cells experimentation at wastewater treatment plant Milano-Nosedo, *International Journal of Hydrogen Energy* 40 (2015) 14683-14689.
- [18] R. Rousseau, X. Dominguez-Benetton, M.-L. Délia, A. Bergel, Microbial bioanodes with high salinity tolerance for microbial fuel cells and microbial electrolysis cells, *Electrochemistry Communications* 33 (2013) 1-4.
- [19] S.M. Daud, B.H. Kim, M. Ghasemi, W.R.W. Daud, Separators used in microbial electrochemical technologies: Current status and future prospects, *Bioresource Technology* 195 (2015) 170-179.
- [20] B.R. Dhar, H.S. Lee, Membranes for bioelectrochemical systems: challenges and research advances, *Environmental technology* 34 (2013) 1751-1764.
- [21] R.A. Rozendal, H.V.M. Hamelers, R.J. Molenkamp, C.J.N. Buisman, Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes, *Water research* 41 (2007) 1984-1994.
- [22] J.R. Kim, S. Cheng, S.-E. Oh, B.E. Logan, Power Generation Using Different Cation, Anion, and Ultrafiltration Membranes in Microbial Fuel Cells, *Environmental science & technology* 41 (2007) 1004-1009.
- [23] F. Harnisch, U. Schröder, F. Scholz, The Suitability of Monopolar and Bipolar Ion Exchange Membranes as Separators for Biological Fuel Cells, *Environmental science & technology* 42 (2008) 1740-1746.
- [24] T. Luo, S. Abdu, M. Wessling, Selectivity of ion exchange membranes: A review, *Journal of Membrane Science* 555 (2018) 429-454.
- [25] M. Oliot, S. Galier, H. Roux de Balman, A. Bergel, Ion transport in microbial fuel cells: Key roles, theory and critical review, *Applied Energy* 183 (2016) 1682-1704.

- [26] F. Harnisch, U. Schröder, Selectivity versus Mobility: Separation of Anode and Cathode in Microbial Bioelectrochemical Systems, *ChemSusChem* 2 (2009) 921-926.
- [27] S.C. Popat, D. Ki, M.N. Young, B.E. Rittmann, C.I. Torres, Buffer pKa and Transport Govern the Concentration Overpotential in Electrochemical Oxygen Reduction at Neutral pH, *ChemElectroChem* 1 (2014) 1909-1915.
- [28] C.I. Torres, A. Kato Marcus, B.E. Rittmann, Proton transport inside the biofilm limits electrical current generation by anode-respiring bacteria, *Biotechnology and bioengineering* 100 (2008) 872-881.
- [29] M. Dopson, G. Ni, T.H. Sleutels, Possibilities for extremophilic microorganisms in microbial electrochemical systems, *FEMS Microbiology Reviews* 40 (2015) 164-181.
- [30] G.C. Gil, I.S. Chang, B.H. Kim, M. Kim, J.K. Jang, H.S. Park, H.J. Kim, Operational parameters affecting the performance of a mediator-less microbial fuel cell, *Biosensors & bioelectronics* 18 (2003) 327-334.
- [31] O. Gutierrez, D. Park, K.R. Sharma, Z. Yuan, Effects of long-term pH elevation on the sulfate-reducing and methanogenic activities of anaerobic sewer biofilms, *Water research* 43 (2009) 2549-2557.
- [32] H. Hiegemann, T. Littfinski, S. Krimmler, M. Lübken, D. Klein, K.-G. Schmelz, K. Ooms, D. Pant, M. Wichern, Performance and inorganic fouling of a submersible 255 L prototype microbial fuel cell module during continuous long-term operation with real municipal wastewater under practical conditions, *Bioresource Technology* 294 (2019) 122227.
- [33] J. Ma, Z. Wang, D. Suor, S. Liu, J. Li, Z. Wu, Temporal variations of cathode performance in air-cathode single-chamber microbial fuel cells with different separators, *Journal of Power Sources* 272 (2014) 24-33.
- [34] G.H. Rau, Electrochemical Splitting of Calcium Carbonate to Increase Solution Alkalinity: Implications for Mitigation of Carbon Dioxide and Ocean Acidity, *Environmental science & technology* 42 (2008) 8935-8940.

- [35] M.M. Tlili, M. Benamor, C. Gabrielli, H. Perrot, B. Tribollet, Influence of the Interfacial pH on Electrochemical CaCO₃ Precipitation, *Journal of The Electrochemical Society* 150 (2003) C765.
- [36] B. Erable, R. Lacroix, L. Etcheverry, D. Féron, M.L. Delia, A. Bergel, Marine floating microbial fuel cell involving aerobic biofilm on stainless steel cathodes, *Bioresource Technology* 142 (2013) 510-516.
- [37] R.A. Rozendal, H.V. Hamelers, C.J. Buisman, Effects of membrane cation transport on pH and microbial fuel cell performance, *Environmental science & technology* 40 (2006) 5206-5211.
- [38] C.I. Torres, H.-S. Lee, B.E. Rittmann, Carbonate Species as OH⁻ Carriers for Decreasing the pH Gradient between Cathode and Anode in Biological Fuel Cells, *Environmental science & technology* 42 (2008) 8773-8777.
- [39] T.H.J.A. Sleutels, H.V.M. Hamelers, R.A. Rozendal, C.J.N. Buisman, Ion transport resistance in Microbial Electrolysis Cells with anion and cation exchange membranes, *International Journal of Hydrogen Energy* 34 (2009) 3612-3620.
- [40] U. Schroder, F. Harnisch, L.T. Angenent, Microbial electrochemistry and technology: terminology and classification, *Energy & Environmental Science* 8 (2015) 513-519.
- [41] S. Bajracharya, R. Yuliasni, K. Vanbroekhoven, C.J.N. Buisman, D.P.B.T.B. Strik, D. Pant, Long-term operation of microbial electrosynthesis cell reducing CO₂ to multi-carbon chemicals with a mixed culture avoiding methanogenesis, *Bioelectrochemistry* 113 (2017) 26-34.
- [42] S. Kondaveeti, I.M. Abu-Reesh, G. Mohanakrishna, M. Bulut, D. Pant, Advanced Routes of Biological and Bio-electrocatalytic Carbon Dioxide (CO₂) Mitigation Toward Carbon Neutrality, *Frontiers in Energy Research* 8 (2020).

- [43] A. Schievano, D. Pant, S. Puig, Editorial: Microbial Synthesis, Gas-Fermentation and Bioelectroconversion of CO₂ and Other Gaseous Streams, *Frontiers in Energy Research* 7 (2019).
- [44] R. Takors, M. Kopf, J. Mampel, W. Bluemke, B. Blombach, B. Eikmanns, F.R. Bengelsdorf, D. Weuster-Botz, P. Dürre, Using gas mixtures of CO, CO₂ and H₂ as microbial substrates: the do's and don'ts of successful technology transfer from laboratory to production scale, *Microb Biotechnol* 11 (2018) 606-625.
- [45] X. Christodoulou, T. Okoroafor, S. Parry, S.B. Velasquez-Orta, The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility, *Journal of CO₂ Utilization* 18 (2017) 390-399.
- [46] K.P. Nevin, T.L. Woodard, A.E. Franks, Z.M. Summers, D.R. Lovley, Microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds, *mBio* 1 (2010).
- [47] G. Zhen, X. Lu, G. Kumar, P. Bakonyi, K. Xu, Y. Zhao, Microbial electrolysis cell platform for simultaneous waste biorefinery and clean electrofuels generation: Current situation, challenges and future perspectives, *Progress in Energy and Combustion Science* 63 (2017) 119-145.
- [48] B. Bian, S. Bajracharya, J. Xu, D. Pant, P.E. Saikaly, Microbial electrosynthesis from CO₂: Challenges, opportunities and perspectives in the context of circular bioeconomy, *Bioresource Technology* 302 (2020) 122863.
- [49] S. Srikanth, D. Singh, K. Vanbroekhoven, D. Pant, M. Kumar, S.K. Puri, S.S.V. Ramakumar, Electro-biocatalytic conversion of carbon dioxide to alcohols using gas diffusion electrode, *Bioresource Technology* 265 (2018) 45-51.
- [50] R.A. Tufa, D. Chanda, M. Ma, D. Aili, T.B. Demissie, J. Vaes, Q. Li, S. Liu, D. Pant, Towards highly efficient electrochemical CO₂ reduction: Cell designs, membranes and electrocatalysts, *Applied Energy* 277 (2020) 115557.

- [51] S. Bajracharya, B. van den Burg, K. Vanbroekhoven, H. De Wever, C.J.N. Buisman, D. Pant, D.P.B.T.B. Strik, In situ acetate separation in microbial electrosynthesis from CO₂ using ion-exchange resin, *Electrochimica Acta* 237 (2017) 267-275.
- [52] G. Mohanakrishna, I.M. Abu Reesh, K. Vanbroekhoven, D. Pant, Microbial electrosynthesis feasibility evaluation at high bicarbonate concentrations with enriched homoacetogenic biocathode, *The Science of the total environment* 715 (2020) 137003.
- [53] B.H. Yan, A. Selvam, S.Y. Xu, J.W.C. Wong, A novel way to utilize hydrogen and carbon dioxide in acidogenic reactor through homoacetogenesis, *Bioresource Technology* 159 (2014) 249-257.
- [54] M. Zeppilli, H. Chouchane, L. Scardigno, M. Mahjoubi, M. Gacitua, R. Askri, A. Cherif, M. Majone, Bioelectrochemical vs hydrogenophilic approach for CO₂ reduction into methane and acetate, *Chemical Engineering Journal* 396 (2020) 125243.
- [55] M. Zeppilli, I. Ceccarelli, M. Villano, M. Majone, Reduction of carbon dioxide into acetate in a fully biological microbial electrolysis cell, *Chemical Engineering Transactions*, 2016, pp. 445-450.
- [56] H.D. May, P.J. Evans, E.V. LaBelle, The bioelectrosynthesis of acetate, *Current opinion in biotechnology* 42 (2016) 225-233.
- [57] S.J. Andersen, T. Hennebel, S. Gildemyn, M. Coma, J. Desloover, J. Berton, J. Tsukamoto, C. Stevens, K. Rabaey, Electrolytic Membrane Extraction Enables Production of Fine Chemicals from Biorefinery Sidestreams, *Environmental science & technology* 48 (2014) 7135-7142.
- [58] S. Gildemyn, K. Verbeeck, R. Slabbinck, S.J. Andersen, A. PrévotEAU, K. Rabaey, Integrated Production, Extraction, and Concentration of Acetic Acid from CO₂ through Microbial Electrosynthesis, *Environmental Science & Technology Letters* 2 (2015) 325-328.
- [59] K. Verbeeck, S. Gildemyn, K. Rabaey, Membrane Electrolysis Assisted Gas Fermentation for Enhanced Acetic Acid Production, *Frontiers in Energy Research* 6 (2018).

- [60] I. Vassilev, P.A. Hernandez, P. Batlle-Vilanova, S. Freguia, J.O. Krömer, J. Keller, P. Ledezma, B. Viridis, Microbial Electrosynthesis of Isobutyric, Butyric, Caproic Acids, and Corresponding Alcohols from Carbon Dioxide, *ACS Sustainable Chemistry & Engineering* 6 (2018) 8485-8493.
- [61] I. Vassilev, F. Kracke, S. Freguia, J. Keller, J.O. Krömer, P. Ledezma, B. Viridis, Microbial electrosynthesis system with dual biocathode arrangement for simultaneous acetogenesis, solventogenesis and carbon chain elongation, *Chemical Communications* 55 (2019) 4351-4354.
- [62] D. Andriani, A. Wresta, T.D. Atmaja, A. Saepudin, A review on optimization production and upgrading biogas through CO₂ removal using various techniques, *Applied biochemistry and biotechnology* 172 (2014) 1909-1928.
- [63] F. Bauer, T. Persson, C. Hulteberg, D. Tamm, Biogas upgrading – technology overview, comparison and perspectives for the future, *Biofuels, Bioproducts and Biorefining* 7 (2013) 499-511.
- [64] I. Angelidaki, P. Lyhne, G. Luo, Methods and apparatus for hydrogen based biogas upgrading, Google Patents, 2013.
- [65] N. Aryal, T. Kvist, F. Ammam, D. Pant, L.D.M. Ottosen, An overview of microbial biogas enrichment, *Bioresource Technology* 264 (2018) 359-369.
- [66] M.A. Voelklein, D. Rusmanis, J.D. Murphy, Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion, *Applied Energy* 235 (2019) 1061-1071.
- [67] S. Cheng, D. Xing, D.F. Call, B.E. Logan, Direct biological conversion of electrical current into methane by electromethanogenesis, *Environmental Science and Technology* 43 (2009) 3953-3958.
- [68] S. Cheng, B. Logan, Electromethanogenic reactor and processes for methane production, Google Patents, 2013.

- [69] M. Villano, F. Aulenta, A. Giuliano, C. Ciucci, T. Ferri, M. Majone, Bioelectrochemical reduction of CO₂ to CH₄ via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture, *Bioresource Technology* 101 (2010) 3085-3090.
- [70] R. Blasco-Gómez, P. Batlle-Vilanova, M. Villano, M. Balaguer, J. Colprim, S. Puig, On the Edge of Research and Technological Application: A Critical Review of Electromethanogenesis, *International Journal of Molecular Sciences* 18 (2017) 874.
- [71] F. Geppert, D. Liu, M. van Eerten-Jansen, E. Weidner, C. Buisman, A. ter Heijne, Bioelectrochemical Power-to-Gas: State of the Art and Future Perspectives, *Trends in biotechnology* 34 (2016) 879-894.
- [72] Z. Dou, C.M. Dykstra, S.G. Pavlostathis, Bioelectrochemically assisted anaerobic digestion system for biogas upgrading and enhanced methane production, *Science of The Total Environment* 633 (2018) 1012-1021.
- [73] K. Verbeeck, J. De Vrieze, M. Biesemans, K. Rabaey, Membrane electrolysis-assisted CO₂ and H₂S extraction as innovative pretreatment method for biological biogas upgrading, *Chemical Engineering Journal* (2018).
- [74] Y. Zhang, I. Angelidaki, Innovative self-powered submersible microbial electrolysis cell (SMEC) for biohydrogen production from anaerobic reactors, *Water research* 46 (2012) 2727-2736.
- [75] Y. Zhang, I. Angelidaki, Microbial electrolysis cells turning to be versatile technology: Recent advances and future challenges, *Water research* 56 (2014) 11-25.
- [76] I. Bassani, P.G. Kougias, I. Angelidaki, In-situ biogas upgrading in thermophilic granular UASB reactor: key factors affecting the hydrogen mass transfer rate, *Bioresource Technology* 221 (2016) 485-491.
- [77] G. Luo, I. Angelidaki, Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture, *Biotechnology and bioengineering* 109 (2012) 2729-2736.

- [78] M. Villano, S. Scardala, F. Aulenta, M. Majone, Carbon and nitrogen removal and enhanced methane production in a microbial electrolysis cell, *Bioresource Technology* 130 (2013) 366-371.
- [79] P. Batlle-Vilanova, S. Puig, R. Gonzalez-Olmos, A. Vilajeliu-Pons, M.D. Balaguer, J. Colprim, Deciphering the electron transfer mechanisms for biogas upgrading to biomethane within a mixed culture biocathode, *RSC Advances* 5 (2015) 52243-52251.
- [80] H. Xu, K. Wang, D.E. Holmes, Bioelectrochemical removal of carbon dioxide (CO₂): An innovative method for biogas upgrading, *Bioresource Technology* 173 (2014) 392-398.
- [81] M. Zeppilli, A. Lai, M. Villano, M. Majone, Anion vs cation exchange membrane strongly affect mechanisms and yield of CO₂ fixation in a microbial electrolysis cell, *Chemical Engineering Journal* 304 (2016) 10-19.
- [82] M. Villano, F. Aulenta, M. Majone, Perspectives of biofuels production from renewable resources with bioelectrochemical systems, *Asia-Pacific Journal of Chemical Engineering* 7 (2012) S263-S274.
- [83] M. Villano, C. Ralo, M. Zeppilli, F. Aulenta, M. Majone, Influence of the set anode potential on the performance and internal energy losses of a methane-producing microbial electrolysis cell, *Bioelectrochemistry* 107 (2016) 1-6.
- [84] M. Zeppilli, A. Mattia, M. Villano, M. Majone, Three-chamber Bioelectrochemical System for Biogas Upgrading and Nutrient Recovery, *Fuel Cells* 17 (2017) 593-600.
- [85] M. Zeppilli, M. Simoni, P. Paiano, M. Majone, Two-side cathode microbial electrolysis cell for nutrients recovery and biogas upgrading, *Chemical Engineering Journal* 370 (2019) 466-476.
- [86] M. Zeppilli, L. Cristiani, E. Dell'Armi, M. Majone, Bioelectromethanogenesis reaction in a tubular Microbial Electrolysis Cell (MEC) for biogas upgrading, *Renewable Energy* 158 (2020) 23-31.

- [87] L. Cristiani, M. Zeppilli, C. Porcu, M. Majone, Ammonium Recovery and Biogas Upgrading in a Tubular Micro-Pilot Microbial Electrolysis Cell (MEC), *Molecules* 25 (2020) 2723.
- [88] A. Kokkoli, Y. Zhang, I. Angelidaki, Microbial electrochemical separation of CO₂ for biogas upgrading, *Bioresource Technology* 247 (2018) 380-386.
- [89] K. Kugler, B. Ohs, M. Scholz, M. Wessling, Towards a carbon independent and CO₂-free electrochemical membrane process for NH₃ synthesis, *Physical Chemistry Chemical Physics* 16 (2014) 6129-6138.
- [90] J.W. Erisman, T.A. Larsen, Nitrogen economy of the 21st century, *Source Separation and Decentralization for Wastewater Management*. London: IWA Publishing (2013) 45-58.
- [91] B. Viridis, K. Rabaey, Z. Yuan, J. Keller, Microbial fuel cells for simultaneous carbon and nitrogen removal, *Water research* 42 (2008) 3013-3024.
- [92] R. Cord-Ruwisch, Y. Law, K.Y. Cheng, Ammonium as a sustainable proton shuttle in bioelectrochemical systems, *Bioresource Technology* 102 (2011) 9691-9696.
- [93] P.T. Kelly, Z. He, Nutrients removal and recovery in bioelectrochemical systems: A review, *Bioresour Technol* 153 (2014) 351-360.
- [94] M. Cerrillo, M. Viñas, A. Bonmatí, Removal of volatile fatty acids and ammonia recovery from unstable anaerobic digesters with a microbial electrolysis cell, *Bioresource Technology* 219 (2016) 348-356.
- [95] X. Wu, O. Modin, Ammonium recovery from reject water combined with hydrogen production in a bioelectrochemical reactor, *Bioresource Technology* 146 (2013) 530-536.
- [96] M. Zeppilli, D. Pavesi, M. Gottardo, F. Micolucci, M. Villano, M. Majone, Using effluents from two-phase anaerobic digestion to feed a methane-producing microbial electrolysis, *Chemical Engineering Journal* 328 (2017) 428-433.

- [97] X. Cao, X. Huang, P. Liang, K. Xiao, Y. Zhou, X. Zhang, B.E. Logan, A new method for water desalination using microbial desalination cells, *Environmental Science and Technology* 43 (2009) 7148-7152.
- [98] A. Al-Mamun, W. Ahmad, M.S. Baawain, M. Khadem, B.R. Dhar, A review of microbial desalination cell technology: Configurations, optimization and applications, *Journal of Cleaner Production* 183 (2018) 458-480.
- [99] P. Ledezma, J. Jermakka, J. Keller, S. Freguia, Recovering Nitrogen as a Solid without Chemical Dosing: Bio-Electroconcentration for Recovery of Nutrients from Urine, *Environmental Science & Technology Letters* 4 (2017) 119-124.
- [100] Y. Zhang, I. Angelidaki, A new method for in situ nitrate removal from groundwater using submerged microbial desalination–denitrification cell (SMDDC), *Water research* 47 (2013) 1827-1836.
- [101] P. Kuntke, K.M. Śmiech, H. Bruning, G. Zeeman, M. Saakes, T.H.J.A. Sleutels, H.V.M. Hamelers, C.J.N. Buisman, Ammonium recovery and energy production from urine by a microbial fuel cell, *Water research* 46 (2012) 2627-2636.
- [102] J. Desloover, A. Abate Woldeyohannis, W. Verstraete, N. Boon, K. Rabaey, Electrochemical Resource Recovery from Digestate to Prevent Ammonia Toxicity during Anaerobic Digestion, *Environmental science & technology* 46 (2012) 12209-12216.
- [103] S. Haddadi, G. Nabi-Bidhendi, N. Mehrdadi, Nitrogen removal from wastewater through microbial electrolysis cells and cation exchange membrane, *Journal of environmental health science & engineering* 12 (2014) 48.
- [104] C. Vaneckhaute, V. Lebuf, E. Michels, E. Belia, P.A. Vanrolleghem, F.M.G. Tack, E. Meers, Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification, *Waste and Biomass Valorization* 8 (2017) 21-40.

- [105] P. Ledezma, P. Kuntke, C.J.N. Buisman, J. Keller, S. Freguia, Source-separated urine opens golden opportunities for microbial electrochemical technologies, *Trends in biotechnology* 33 (2015) 214-220.
- [106] E.-L. Viskari, G. Grobler, K. Karimäki, A. Gorbatova, R. Vilpas, S. Lehtoranta, Nitrogen Recovery With Source Separation of Human Urine—Preliminary Results of Its Fertiliser Potential and Use in Agriculture, *Frontiers in Sustainable Food Systems* 2 (2018).
- [107] I. Ieropoulos, J. Greenman, C. Melhuish, Urine utilisation by microbial fuel cells; energy fuel for the future, *Physical Chemistry Chemical Physics* 14 (2012) 94-98.
- [108] P. Kuntke, T.H.J.A. Sleutels, M. Saakes, C.J.N. Buisman, Hydrogen production and ammonium recovery from urine by a Microbial Electrolysis Cell, *International Journal of Hydrogen Energy* 39 (2014) 4771-4778.
- [109] T.H. Muster, J. Jermakka, Electrochemically-assisted ammonia recovery from wastewater using a floating electrode, *Water Science and Technology* 75 (2017) 1804-1811.
- [110] R.W. Scholz, A.E. Ulrich, M. Eilittä, A. Roy, Sustainable use of phosphorus: A finite resource, *Science of The Total Environment* 461-462 (2013) 799-803.
- [111] D. Cordell, J.-O. Drangert, S. White, The story of phosphorus: Global food security and food for thought, *Global Environmental Change* 19 (2009) 292-305.
- [112] B.E. Rittmann, B. Mayer, P. Westerhoff, M. Edwards, Capturing the lost phosphorus, *Chemosphere* 84 (2011) 846-853.
- [113] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review, *Critical Reviews in Environmental Science and Technology* 39 (2009) 433-477.
- [114] F. Fischer, C. Bastian, M. Happe, E. Mabillard, N. Schmidt, Microbial fuel cell enables phosphate recovery from digested sewage sludge as struvite, *Bioresource Technology* 102 (2011) 5824-5830.

- [115] R.D. Cusick, B.E. Logan, Phosphate recovery as struvite within a single chamber microbial electrolysis cell, *Bioresource Technology* 107 (2012) 110-115.
- [116] K. Hirooka, O. Ichihashi, Phosphorus recovery from artificial wastewater by microbial fuel cell and its effect on power generation, *Bioresource Technology* 137 (2013) 368-375.
- [117] G.-L. Zang, G.-P. Sheng, W.-W. Li, Z.-H. Tong, R.J. Zeng, C. Shi, H.-Q. Yu, Nutrient removal and energy production in a urine treatment process using magnesium ammonium phosphate precipitation and a microbial fuel cell technique, *Physical Chemistry Chemical Physics* 14 (2012) 1978-1984.
- [118] F. Fischer, G. Zufferey, M. Sugnaux, M. Happe, Microbial electrolysis cell accelerates phosphate remobilisation from iron phosphate contained in sewage sludge, *Environmental Sciences: Processes and Impacts* 17 (2015) 90-97.
- [119] M. Happe, M. Sugnaux, C.P. Cachelin, M. Stauffer, G. Zufferey, T. Kahoun, P.-A. Salamin, T. Egli, C. Comninellis, A.-F. Grogg, F. Fischer, Scale-up of phosphate remobilization from sewage sludge in a microbial fuel cell, *Bioresource Technology* 200 (2016) 435-443.
- [120] K. Rabaey, S. Bützer, S. Brown, J. Keller, R.A. Rozendal, High Current Generation Coupled to Caustic Production Using a Lamellar Bioelectrochemical System, *Environmental science & technology* 44 (2010) 4315-4321.
- [121] M.A. Arugula, K.S. Brastad, S.D. Minteer, Z. He, Enzyme catalyzed electricity-driven water softening system, *Enzyme and Microbial Technology* 51 (2012) 396-401.
- [122] M. Perumalsamy, Microbial Desalination Cell: An Integrated Technology for Desalination, Wastewater Treatment and Renewable Energy Generation, *Materials Research Foundations* 46.
- [123] K.S. Brastad, Z. He, Water softening using microbial desalination cell technology, *Desalination* 309 (2013) 32-37.

- [124] P. Clauwaert, J. De Paepe, F. Jiang, B. Alonso-Fariñas, E. Vaiopoulou, A. Verliefde, K. Rabaey, Electrochemical tap water softening: A zero chemical input approach, *Water research* 169 (2020) 115263.
- [125] T. Hvitved-Jacobsen, J. Vollertsen, A.H. Nielsen, *Sewer processes: microbial and chemical process engineering of sewer networks*, CRC press 2013.
- [126] I. Pikaar, K.R. Sharma, S. Hu, W. Gernjak, J. Keller, Z. Yuan, Reducing sewer corrosion through integrated urban water management, *Science* 345 (2014) 812-814.
- [127] H. Lin, W. Liu, X. Zhang, N. Williams, B. Hu, Microbial electrochemical septic tanks (MESTs): An alternative configuration with improved performance and minimal modifications on conventional septic systems, *Biochemical Engineering Journal* 120 (2017) 146-156.
- [128] I. Pikaar, M. Flugel, H.-W. Lin, S. Salehin, J. Li, B.C. Donose, P.G. Dennis, L. Bethke, I. Johnson, K. Rabaey, Z. Yuan, Full-scale investigation of in-situ iron and alkalinity generation for efficient sulfide control, *Water research* 167 (2019) 115032.
- [129] J.M. Campos-Martin, G. Blanco-Brieva, J.L. Fierro, Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process, *Angewandte Chemie* 45 (2006) 6962-6984.
- [130] P.C. Foller, R.T. Bombard, Processes for the production of mixtures of caustic soda and hydrogen peroxide via the reduction of oxygen, *Journal of Applied Electrochemistry* 25 (1995) 613-627.
- [131] R.A. Rozendal, E. Leone, J. Keller, K. Rabaey, Efficient hydrogen peroxide generation from organic matter in a bioelectrochemical system, *Electrochemistry Communications* 11 (2009) 1752-1755.
- [132] M. Qin, C. White, S. Zou, Z. He, Passive separation of recovered ammonia from catholyte for reduced energy consumption in microbial electrolysis cells, *Chemical Engineering Journal* 334 (2018) 2303-2307.

[133] P. Zamora, T. Georgieva, A. Ter Heijne, T.H.J.A. Sleutels, A.W. Jeremiasse, M. Saakes, C.J.N. Buisman, P. Kuntke, Ammonia recovery from urine in a scaled-up Microbial Electrolysis Cell, *Journal of Power Sources* 356 (2017) 491-499.

[134] P.K. Dutta, K. Rabaey, Z. Yuan, R.A. Rozendal, J. Keller, Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent, *Water research* 44 (2010) 2563-2571.