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

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Abstract

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

Keywords: Bioelectrochemical systems, secondary Microbial Electrochemical Technologies (METs), ammonia recovery, phosphorus recovery, biogas upgrading, water softening
1. Introduction: Ionic charge transport and pH split generation in bioelectrochemical systems

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

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

\[
J_i = J_{\text{diff,}i} + J_{\text{mig,}i} = -D_i \frac{\partial C_i}{\partial z} - \frac{z_i F}{R T} D_i C_i \frac{\partial V}{\partial z} \tag{1}
\]

where,

- \( D_i \) = diffusion coefficient of the ion \( i \) (cm² sec⁻¹)
- \( C_i \) = concentration of the ion \( i \) (mmol cm⁻³),
Each ion present in the medium contributes to this migration. According to the transference
number, the fraction of this contribution of migration flux for a specific ion is dependent on
its charge, concentration, and diffusion coefficient [12]:

\[
\eta_i = \frac{J_{\text{mig},i}}{J_{\text{mig}}} = \frac{|z_i|^2 D_i C_i}{\sum_k |z_k|^2 D_k C_k}
\] (5)

where \( J_{\text{mig}} \) refers to the total migration flux. In a conventional abiotic electrochemical
process, such as the water electrolysis, a high concentration of ionic species is used to
ensure a good conductivity (i.e. 10–33% KOH solution is used to obtain a conductivity of up
to 60 S/m in available water electrolyzers). In the BESs, the electrolytes are neutral solutions
optimized for the biofilm growth [15], which is however characterized by a low ionic
conductivity due the low tolerance of many microorganisms to high salinities [16-18]. Under
these conditions, the concentration of the proton is 10^{-4} \text{mM}, whereas other cations and
anions (e.g., Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) are usually 10^5 times more concentrated. This
leads to a variety of ions being transported through migration forces in BESs.

Different strategies can be adopted to guarantee the electroneutrality maintenance while
separating anode and cathode, which include the use of ion exchange membranes (IEM)
[19, 20], non-porous membrane for the selective transport of cations (cation exchange
membranes, CEM) [21], anions (anion exchange membranes, AEM) [22] or both cations
and anions (bipolar exchange membranes, BPM) [23]. Both CEMs and AEMs are
characterized by fixed charges that create a high selectivity for the respective charge it is
intended to transport. In other words, the transference number for counter ions is very low,
allowing a selective migration across the membrane. The permselectivity is the ion
selectivity between counter- and co-ions; it represents the most important property of IEMs.
regulating the coulombic and energy efficiency of the electrochemical process. In general, the resistance of a IEMs depends on the chemical structure and its permselectivity \[a\]. Usually, for commercially available membranes, constituted by a homogeneous polymer, resistivity (i.e. area resistance normalized by film thickness) is measured using a dilute NaCl solution which is not representative of a real process operation \[b\]. Several authors developed different experimental methods to determine the IEMs resistance which includes the use of direct polarization methods or impedance spectroscopy \[c\]. The membrane resistance strongly depends on the concentration and composition of the electrolytic solutions in contact with the membrane because it determines the water uptake and ionic concentration profile in the membrane (i.e. Donnan equilibrium). The presence of concentrated multispecies electrolytes promotes an increase in the resistance of the IEMs which is explained by the lower activity of the ions present in the membrane with respect the ions present in the bulk electrolytic solution \[d\]. As a consequence, the lower ions activity in the membrane promotes the lowering of water fraction in the membrane (i.e. membrane shrinking) which induce a consequent constrict of hydrophilic channels for the ions transport \[e\]. As reported in some studies, cation exchange membranes (CEM) resistance generally resulted higher with respect anion exchange membranes (AEM) due to the difference in ion mobility, which indicates the dependence of the IEMs resistance by the ionic species concentration in the electrolytes \[f\]. Indeed, more detailed investigations clarified the reason of the higher resistance in the CEM thank to the determination of the transported species under cationic and anionic transport \[g\]. Being the OH- species the most commonly transported charge through the AEM, a lower gradient between membrane and bulk solutions was obtained determining a lower resistance of the AEM membrane. On the contrary, in the CEM membrane most of the ionic charge was transported by other species than protons, which promote an increase of membrane solution concentration gradient and ionic resistance \[h\]. In cases where Ohmic overpotentials have been characterized in BESs,
their value was often \(< 10\%\) of the total overpotentials, while potential losses associated to the pH split where much larger \([ac]\)." A good example of permselectivity regulation is offered by the work conducted on chloroalkali process in which several studies focused their attention to the control and reduction the OH\(^-\) transport through the CEM during the chloroalkali process by the presence of the perfluorosulphonic polymer providing a good OH\(^-\) blocking capacity [24].

As already mentioned, the use of IEMs, which transport cations and anions other than protons and hydroxyls, results in the pH splitting between the anodic and cathodic compartment of a BESs due to the ion transfer through the electrolyte and the IEM [25]. When looked in detail, the pH split between anode and cathode involves both CEM and AEM separators, and it is mainly related to the higher concentration of other ionic species, which compete with protons and hydroxyl ions [26, 27]. As reported in Fig.1, the migration of ionic species being different from protons and hydroxyls at neutral pH more favorable due to their higher concentrations, mostly of the charged is transported by species which do not participate to the oxidation and reduction reactions. The continuous production of protons in the anode and its simultaneous consumption by the reduction reaction at the cathode generates an accumulation of protons in the anolyte (acidification) and an accumulation of hydroxyl ions at the cathode (alkalization) coming from water autoproteolysis.
Alkali and acid production through the transport of ionic species is influenced by several parameters such as electrolytes composition, membrane permselectivity and current density. Even if similar modelling approaches for bioelectrochemical systems [I, II], which involved the use of the mass and electron balances along with the equations that describes the ion transport through an ion exchange membrane, have been described in the literature, a comprehensive model which describes the pH split phenomenon has not yet described. The most recent models adopted the assumption of an infinite fast acid-base reactions which makes numerical analysis much easier [III]. By the infinite fast rate assumption, already described in the literature, all the fluxes of the ions and the pH profile during the bioelectrochemical cell operation have been described [IV].
While anions and cations are transported across the selective IEMs or blocked as counter ion (depending on the type of IEMs adopted), even uncharged molecules can also be transported by diffusional phenomena through the IEMs. Uncharged species being transported only by diffusional forces, while the uncharged molecules are not influenced by the electric field and the fixed charge groups present on the ion exchange membrane surface. However, even if the diffusion of uncharged molecules is not correlated to the electrons flow in the bioelectrochemical device, the diffusion of uncharged molecules can influence the bioelectrochemical reactions coulombic efficiency. As reported in the literature, the diffusion of organic substrates from a COD oxidizing bioanode to a methanogenic biocathode improved methane generation by the activation of acetolactic pathways, which did not include electroactive microorganisms leading to an overestimation of the efficiency of the bioelectrochemical reaction [i]. The acidification of the anodic chamber and the alkalization of the cathodic one promotes two main disadvantages for the process operation; the first one is linked to the biofilm stability, while the energy loss due to the pH gradient decreases the power output or the power consumption of a bioelectrochemical process for the microbial fuel cell (MFC) and microbial electrolysis cell (MEC), respectively [28]. The anodic oxidation reaction releases protons, which provoke a local acidification near the anodic surface; this local acidification decrease severely affects the microorganisms’ activity, limiting the electrocatalytic activity of the biofilms [29, 30]. The cathode reduction reaction consumes protons (or releases hydroxides), causing the alkalization of the chamber. Alkalization also decreases the microorganisms’ activity, promoting a partial or complete inhibition of the biofilm [31]. Moreover, other possible effects related to the pH increase are the precipitation of cations like Ca$^{2+}$ or Mg$^{2+}$ on the surface of cathode, which promotes the surface fouling of the cathodic material [32-35]. The fouling of the cathodic material is particularly disadvantageous in benthic MFCs because of the increased
concentrations of earth alkaline cation species in seawater [36]. In terms of electrochemical losses, the pH split between anode and cathode promotes the creation of an additional overpotential related to the different proton concentrations; the pH gradient develops over the membrane, causing further potential drop of about 59 mV for each unit of pH [37].

The ion migration through the electrolytes and the IEM depends on the reaction rates of the bioelectrochemical reactions, which is described by the current density; an increase in the current density is linked to the acidity and alkalinity generation in the two compartments of a BESs. The consequent pH split is an undesirable condition of the MFC that negatively affects the energy output and the long-term stability of the process. In order to mitigate the pH split in the MFC devices, several researchers proposed the utilization of different separators including IEMs, porous membrane and bio-separators along with the maintenance of the separation of the electrolytes between the anodic and the cathodic compartments. Alternatively, researchers have proposed the addition of an acid on the cathode, such as CO$_2$, to mitigate the pH gradient and associated potential loss [38].

Differently, the energy losses in a MEC due to the ionic transport and the pH split introduce an additional energy consumption of the system, which is generally a disadvantageous effect [39]. However, with a new conceptual view, the pH split in a MEC results in an advantageous phenomenon that can be used for several environmental applications. This review summarizes the different bioelectrochemical applications in which pH split phenomenon and the associated effects are exploited for environmental applications including the recovery of CO$_2$ electrosynthesis products, the nutrient recovery, the biogas upgrading, the water desalination/softening and the removal of recalcitrant pollutants. In this frame, the pH split phenomenon can be exploited to control the bioelectrochemical process used for several environmental applications, thanks to the possibility of continuously generating acidity or alkalinity in different compartments. A MEC can be considered as an interesting tool, in which the concept of a secondary microbial electrochemical technology
MET can be realized [40], optimizing the utilization of the electrical energy both for products generation/treatment and for their extraction and refining.

2.1. Products extraction and recovery in bioelectrosynthesis

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

The microbial electrosynthesis (MES) is defined as the utilization of microorganisms in the cathodic chamber of a BESs to produce organic molecules from a CO₂ stream, wherein the electroactive microorganisms are responsible for the electrons transfer and production of chemicals [45-47]. The long-term stability of MES processes and the smart conversion of electricity into CO₂ reduction to products shows good perspectives for the scale up of this technology in the frame of circular economy and added-value products generation [48-50].

Even if several authors reported the possibility to obtain the CO₂ conversion into acetate and other products by pure cultures or mixed microbial consortia [51-54], one of the main bottleneck of the electrosynthesis process is the low product concentration obtained by a simple production approach [55]. The higher acetate production rates reached 3.1 g/L d [56].

Products extraction separation and enrichment results in a major limitation of several biotechnological processes, i.e. it has been estimated that more than 60% of the production costs of the plant should be invested to separate and recover the final products (Bechtold et al 2008). Low cost and efficient separation technologies are highly required in biotechnology industry an interesting approach to overcome the extraction ad purification issue is offered by the “In situ product recovery” (ISPR) which consists in the integration of the production and the separation in the same reactor [r]. Selective membranes are optimal candidate to accomplish the ISPR objectives [s], i.e. several examples of integrated production and extraction approaches have been reported in the literature by the adoption of submerged membranes or in an external configuration creating an external loop process [t,u]. Among membrane processes, the use of ionic exchange membranes in electrodialysis processes constituted an attractive approach being a fast treatment which provides the effective removal of uncharged molecules allowing the simultaneous concentration of the target product [v]. Several electrodialysis applications have been proposed in the literature
for the in-situ lactate recovery to increase lactate concentration and reduce its inhibition
effect of the fermentation broth [Z]. Similarly, the utilization of selective IEMs in in
bioelectrosynthesis processes results an attractive application of the ISPR concept to the
CO₂ fixation into VFAs.
The advantage of the utilization of an electro-microbial technology is offered by the use of
the electrical current to supply the reducing power and the target migration of species due
to the electroneutrality maintenance. In the specific case of the production of a carboxylate,
the use of an AEM promotes the migration of the target products, which in turn can be easily
 protonated by an acid environment, preventing undesired retro diffusion of the products due
to the concentration gradients [57, 58].
A first arrangement which exploited the pH split phenomenon to the acetate extraction via
membrane electrolysis, has been proposed by adopting a conventional two chamber MEC
equipped with an AEM, which promotes the migration of the acetate produced in the cathode
through the abiotic anode [57]. The acetate and the other carboxylates are protonated and
recovered as volatile fatty acids (VFAs) in a clean acidic anolyte due to the acidity production
promoted by the pH split. Moreover, the acetate concentrated at an average concentration
of 14 g/L was converted to ethyl acetate by the addition of ethanol in a separate unit heated
at 70 °C. The integrate bioelectrochemical process allowed for the production of 2.64 g/Lh
to ethyl acetate, with a final total conversion of 58 ± 3%.
The integration of CO₂ reduction into acetate and its in-situ extraction by the electromotive
force, has been also analyzed and modelized by Matemadombo and coworkers, in their
work, two different microbial electrosynthesis cells equipped with an AEM membrane were
utilized for the elaboration and the validation of a mathematical model that described the
simultaneous acetate production and separation from the cathode chamber to the anode
chamber. Despite the low acetate titrate obtained in the two microbial electrosynthesis cells,
the 24% and 18% of the produced acetate migrated from the cathode to the anode
compartments reaching a concentration of 240 mg/L. Based on the mathematical model assumptions, being the flux of acetate from the cathode to the anode proportional to the applied electric potential, acetate migration can be enhanced by increasing the applied potential to the cell [ad].

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

![Diagram of three chamber microbial electrolysis cell](image)

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

During the operation of the three chamber MEC, an average pH of 8.4 was measured in the catholyte, while in the extraction and in the anode compartment an average pH of 1.7 and 2
was determined, respectively. The three chamber MEC concept allows to reach an average acetate production rate of 0.7 g/Ld, accounting for a coulombic efficiency of the cathodic reaction of 76%, while in the first operational cycle an extraction rate of 22 g/m²d, corresponding to a recovery efficiency of 99%, was obtained. The three chamber MEC allowed to obtain an acetate solution with an average concentration of 13 g/L, showing the concentration potential of the three chamber MEC controlled by the pH split phenomenon. It is noteworthy to mention that as reported by the authors, during a failure in the CO₂ supply into the cathodic chamber, the catholyte pH sharply increased to 11.6 due to lack of buffer effect promoted by the CO₂ dissolution; this demonstrates the important effect of the pH split phenomenon, which results by the adoption of almost neutral electrolytes. The three chamber MEC concept has been further investigated and optimized with a modified three-chamber MEC concept, in order to optimize the acetate production and extraction by the energetic point of view [59]. As reported by the authors, the extraction efficiency obtained in the previous work was low because of the acetate production rate, which accounted for the 5–8% of the charge balancing. Indeed, as 8 moles electrons are required per mole of acetic acid produced, the protonation and the extraction of the monovalent acetate ion requires one electron; this means that with a 100% coulombic efficiency, only 12.5% of the current can be transported by the acetate anion. It was proposed to run the three chamber MEC by imposing a current to ensure an almost complete coulombic efficiency; thus, an additional reducing power was supplied to the cathodic acetogenic chamber as molecular hydrogen, which was produced by a commercial electrolyzer. By this configuration, a considerable increase in terms of acetate concentration was obtained, reaching 35 g/L of acetate in the extraction chamber. Also, a strong acidic pH was maintained in the anodic and extraction chamber thanks to the transport of different ions instead of protons and hydroxyls. Finally, the study showed that a higher extraction capacity was obtained by suppling an external H₂ source, and indicated that the adoption of a three chamber MEC offers an interesting
approach for both the production and the extraction of a target compounds produced from CO₂. Moreover, the adoption of three chamber MEC configuration can result in an increase of the productivity, coupling the effect of the product removal with the in-situ pH control; the base and acid dosages, which are usually adopted for the pH control of conventional processes to prevent product inhibition and the product stream acidification, are fully replaced by in situ production of hydroxyls (at the cathode) and protons (at the anode). The electrochemical acetate production can be considered a secondary MET, in which the reactor not only provides the reducing power necessary for the electrosynthesis but also increases the process stability and the product extraction through the pH split.

A similar concept, with an innovative two cathode configuration was recently proposed by researchers at AWMC (Australia) focused not only on the acetate production but also in C4-C6 carboxylic acids. It was reported that, maintaining a slightly acidic pH in the cathodic chamber of a biocathode can result in the solventogenesis, promoting the production of short chain VFAs (e.g. butyrate and caproate) [60]. In this configuration, the pH control in the cathodic chamber was ensured by the CO₂ supply (around the value of 5.4), which is necessary for the methanogenesis inhibition. A new concept of three-chamber electrochemical system, consisting of two biocathodes and one abiotic anodic chamber, has been adopted for the optimization of the acetogenic/chain elongation and solventogenesis step in an integrated bioelectrochemical process [61]. In the new dual cathode reactor, the acetogenesis and chain elongation are kept separated from solventogenesis process and it allows to operate under optimal pH conditions without the addition of chemicals and CO₂ gas sparging. During operation, while the cathode dedicated to the acetogenesis/chain elongation reaction was maintained at pH of 6.9 through the direct CO₂ sparging, in the solventogenesis, the cathodic pH is maintained around the value of 4.9 through the CO₂ bubbling from the biocathode and an alternating control of the electrochemical potential of cathodes.
2.2 Biogas upgrading through BESSs

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

The integration of the AD process and the BM reaction has been proposed as an in-situ approach through the direct insertion of the electrodes into the AD tank; on the other hand, in the ex situ approach, a methane-producing MEC can be used as a post-treatment unit for the biogas treatment [72, 73]. The in-situ approach has been widely explored under laboratory conditions; the reducing power supplied by the cathodic material permits to reach higher methane concentration [74] in the produced biogas, while the oxidation at the anodic
compartment of the soluble COD increases the stability of the AD process with respect the VFAs control [75]. However, the direct insertion of the electrodes in the AD digestor can affect the process stability as the CO₂ conversion into methane can promote the loss of buffering power with a consequent inhibition of the methanogenic activity [76, 77]. Furthermore, the oxidation of the organic compounds performed by anodophilic bacteria using the electrode as electron acceptor, required a lower energy input with respect to the water oxidation reaction. Villano and co-workers, proposed the integration of a fully bio-catalyzed methane producing MEC in cascade combined with an anaerobic digestor; i.e, while the reduction of CO₂ biogas from an anaerobic digestor occurred in the cathode, the anodic oxidation of residual COD content in anaerobic digestate could partially sustain the energy demand of the process; in this frame, the MEC post-treatment could enhance both digestate and biogas quality [78]. Battle-Villanova and co-workers recently proposed a different integration of an AD with a methane producing MEC. The authors proposed to feed the bio-cathode of a MEC with an effluent from a water scrubbing-like unit, where hydrogenophilic methanogens convert the CO₂ into CH₄, instead of directly connecting the MEC to the digester [79]. Xu and co-workers proposed the utilization of methane producing bio-cathode for the reduction of the CO₂ contained in the biogas into additional methane, similar to previously reported studies. Due to CO₂ dissolution in the cathodic chamber, the alkalinity generation increased the upgrading performances [80]. Along with the BM reaction that is responsible for CO₂ reduction into CH₄, the alkalization of the cathodic chamber results in an important additional CO₂ removal mechanism. Considering the CO₂ reduction into CH₄, it is possible to obtain a maximum removal of 9 moles of CO₂ for each mole of CH₄ generated at the cathode according to the following equation [81]:

\[9CO_2 + 8e^- + 6H_2O \rightarrow CH_4 + 8HCO_3^-\]
Another interesting integration of the BM reaction and an AD digestor has been proposed in literature, where a methane-producing MEC works as a post treatment unit of both digestate and biogas [82, 83]. Through the integration of a bioanode and a biocathode, the residual COD content in the digestate partially sustains the energy demand of the process, which is mainly devoted to the CO₂ conversion into CH₄. Another aspect related with the integration of a fully biological MEC and an AD process is the possibility to obtain the ammonium migration and recovery. A three chamber MEC has been also presented as post-treatment unit to refine digestate, to upgrade the biogas and to recover the nutrients like ammonium [84]. In the proposed configuration, the cationic and anionic migration across the membranes, permits the accumulation of ammonium bicarbonate in an intermediate chamber; the three chamber configuration has been developed to combine the ammonium removal from a liquid effluent and the CO₂ removal from a gas in a single device. The three chamber concept has been further optimized by the set-up of two-side cathode configuration, in which the two cathodic compartment, connected in parallel by a titanium wire, maximize the volumetric area of the reactor devoted to the CO₂ removal through the BM reaction and the cathodic alkalinity generation [85]. The two-side cathode promoted a higher CO₂ removal while minimizing the energy consumption of the whole process. The integration of the CO₂ removal for biogas upgrading has been investigated in a scaled-up MEC with a tubular configuration (Fig. 3-A).

In this configuration, the outer biocathode performs the CO₂ removal thanks to the BM reaction and the alkalinity generation; on the contrary, the energetic demand of the process is partially sustained by the bioanode, which bioelectrochemically oxidize the organic matter. A tubular reactor equipped by an AEM has been tested under both potentiostatic three electrode configuration and by a two-electrode configuration polarization. Despite the good CO₂ removal performances, the two-electrode polarization strategy resulted in a higher energy consumption and a limited effect on the CO₂ removal mechanism [86]. Moreover, a
similar reactor configuration equipped with a CEM has been tested for the simultaneous ammonium recovery and CO$_2$ removal (Fig. 3-A).

![Figure 3. Tubular MEC for simultaneous biogas upgrading and ammonium recovery](image)

The CO$_2$ removed using this configuration was higher thanks to the possible migration of Ca$^{2+}$ and Mg$^{2+}$, which introduced another CO$_2$ removal mechanism promoted by the precipitation of insoluble carbonates [87]. The pH split phenomenon that takes place in the anode and the cathode due to the ionic transport has been also exploited in a microbial electrochemical separation cell (MESC), supplied with four compartments and anion and bipolar ion exchange membranes. In this configuration (Fig. 3-B), the pH increase of the adsorption chamber led to the CO$_2$ sorption into HCO$_3^-$, while the pH decrease of the regeneration chamber resulted into the release of CO$_2$ [88].

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

The ammonium migration and diffusion across a PEM/CEM phenomena has been reported by several authors. Virdis and co-workers demonstrated that both migration and diffusion, permits the accumulation of ammonium nitrogen in the cathodic chamber [91]. As mentioned above, in neutral electrolytes involved in bioelectrochemical process (e.g. wastewater), the higher concentrations of ammonium result in a much more favourable migration of ammonium and other cations compared to the protons transportation to maintain the electroneutrality of the system. Cord-Ruwisch demonstrated the exploitation of the ammonium/ammonia as as a proton shuttle, accounting for the 90% of ionic flux in the system, in a two chamber MFC to prevent anolyte acidification [92]. The use of an MFC or a MEC for the ammonium removal/recovery changes the perspectives in terms of energy consumption, i.e. in the MFC a negative energy process allows to the recovery of ammonium
but its performances are negatively influenced by the presence of a strong pH gradient between the anodic and cathodic chamber. On the other hand, even if the use of a MEC requires an energy input, the ammonium recovery rates can be increased by several times resulting in a more efficient strategy for the ammonium recovery and reutilization as a concentrated product [93]. Ammonium migration was also documented in other BESs such as MECs and microbial desalination cells (MDCs) [94, 95]. In a continuous flow MEC aimed at the production of methane, the ammonia migration through a Nafion117 membrane allows for the concentration of ammonium 10 times higher than the influent concentration [78]. By feeding the same MEC with a real effluent coming from the dark fermentation step of a two-stage AD process rich in ammonium, the ammonium migration increases its contribution to the overall electroneutrality maintenance from 2 to 20% [96]. The utilization of MEC for the water desalination has been called MDC, in which the current generated or consumed by electroactive microorganisms promotes the transfer of ionic species out of water [97].

The MDC are composed by three or more chambers separated by different ion exchange membranes, similar to the conventional electrodialysis devices [98]. As previously reported for the CO₂ removal aimed at biogas upgrading, an integrated three chamber MEC has been successfully operated; the CO₂ removal has been coupled with the ammonium recovery, exploiting the current generated by a bioanode. The utilization of a conventional accumulation chamber showed a recovery of an ammonium bicarbonate concentrated solution [84]; in particular, the ammonium migrated from the anodic to the accumulation chamber through a PEM while the CO₂ (from a synthetic biogas adsorbed in the cathode under the HCO₃⁻ form) migrated from the cathodic to the accumulation chamber due to the presence of the AEM. The use of an AEM with a low selectivity allowed the ammonium diffusion from the accumulation to the cathode compartment. The successful recovery of the ammonium ion in one chamber has been overcome by the adoption of a two-side cathode.
configuration (Fig. 4-A), which allowed the integration of CO₂ removal with the ammonium recovery by the bioelectrochemical COD oxidation at lower energy consumption [85].

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

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

Moreover, by the adoption of an MDC type reactor, the ammonium ions can be transferred from the middle to the aerobic cathode compartment for the nitrification step [100]. The possibility to reach the complete ammonium recovery in a BES has been obtained by combining the alkalinity generation in the cathodic chamber with a stripping process. By
using this approach, the ammonia recovery was obtained through catholyte aeration and subsequently ammonia adsorption in an acid solution of a MFC [101]. In addition, the ammonia recovery by catholyte stripping has been investigated as a strategy to mitigate the ammonium inhibition of the AD process, in which the use of a MFC resulted in ammonia removal efficiency of 100% [102]. It has been demonstrated that higher current densities can be exploited to increase the ammonia recovery in an MFC, obtaining a 61% of ammonium transported by electricity-driven migration [103]. The alkaline pH characterizing the cathodic compartment, drives the ammonium to ammonia gas. An application of this interesting aspect has been reported in a study conducted by Wu and Modin, where the recovery of ammonia has been combined with hydrogen production in a MEC treating reject waters [95]. These waters are characterized by high concentration of ammonium (around 1 g/L) but low concentrations of organic compounds. Due to the current generation, a pH increase up to 12 has been detected in the cathodic compartment of the cell, resulting in an ammonia recovery of 96% in the synthetic reject water and 79% in the real reject water. The alkalinisation of the catholyte has been also tested in single chamber MEC for the precipitation of struvite; even if no ion exchange membranes are present in a single chamber configuration, it has been demonstrated that local alkalinisation in the area near the cathodic surface is interesting for the struvite precipitation caused by a local pH increase [104]. The ammonium recovery by ammonia stripping can be adopted as a strategy to increase the recovery efficiency from wastewaters. The ammonium recovery has been deeply investigated in several MDC devices devoted to the recovery of ammonium from urine; several international research actions have been focused on the development of a combined bioelectrochemical process aimed at simultaneously treating the source separated urine and recover not only the ammonium but also elements to reuse as a fertilizer [105, 106]. In the several solutions proposed, the organic load of the urine has been used to generate the electrons driving the ammonium migration. It is noteworthy to observe that the development
chain of the bioelectrochemical technology started from a simple MFC, i.e. urine has been proposed as convenient feed-stream for producing electricity in MFCs [107]. A first MFC using urine as feeding solution resulted in a maximum power output of 0.25 W/m², while a 9.6 gN/m²d were recovered by ammonium migration [101]. Ammonium has been recovered from urine through a MEC tested along with the hydrogen production, showing a recovery rate of 162±10 g/m²d with a cumbic efficiency of 84 ±1% [108]. A MDC cell was operated with a synthetic urine to recover ammonium nitrogen and potassium from urine (Fig. 4-B). The MDC reached a current density of 50 A/m² by controlling the anodic chamber 0.2 V vs SHE, which promoted the removal and the recovery of nitrogen, phosphorous and potassium (average rates of 7.18 kgN/m³d, 0.52 kgP/m³d and 1.62 kgK/m³d, respectively). Moreover, the study reports the possibility to obtain a nitrogen-rich solid in the form of pure NH₄HCO₃ crystals containing 17% of nitrogen by flash-cooling of the obtained concentrate at 4 °C [99]. Another approach has been proposed to electrochemically remove and recover ammonia, exploiting the cathodic alkalinity generated by an electric field, which promoted the ammonium ions migration towards the wastewater-air interface. The ammonia removal and recovery are based on the electrochemical oxidation, and the electrochemically assisted surface transfer mechanism. The ammonia was recovered thanks to the floating electrode approach, without the presence of IEMs [109].

2.4 Phosphorous recovery/remobilization

Phosphorus is an essential element which is mined all over the world and, in particular, on a large scale in the USA, China and Morocco [110]. Phosphorous is a component in synthetic fertilizers and its demand is increasing at 3–4% per year [111]. Phosphorus also represents an important inorganic nutrient and pollutant, mainly recovered by chemical precipitation or biological processes during tertiary treatment in the wastewater treatment plant [112]. For the recovery of the phosphorous, as previous reported for the ammonium,
several studies were conducted on the possibility to use a MFC to obtain the struvite (MgNH$_4$PO$_4$$\cdot$6H$_2$O) precipitation on the cathodic surface of single-chamber devices [113]. This approach permits to stimulate the struvite precipitation thanks to the local alkalinisation that occurs close to the cathodic surface of the cell; even if in a single chamber cell the anolyte and the catholyte are constituted by the same media, mass transfer limitations occurs due to the presence of other ions at significantly higher concentrations, which are responsible for the electroneutrality maintenance [114]. Cusick and Logan demonstrated the possibility of removing up to 40% of soluble phosphate by struvite precipitation (0.3– 0.9 g/m$^2$ h) using a single chamber MFC approach [115]. The single chamber MFC was tested for the recovery of struvite from real waste streams such as swine manure [116] and urine [117]. The MFC removed up to 94% of the soluble phosphorus present in the urine due to the excess of ammonium, while by testing the swine manure a soluble phosphorous removal efficiency of 80% has been determined. Another approach used for the phosphorous recovery by struvite crystallization has been proposed, which includes the use of a two chamber MFC where the bioelectrochemical anodic reaction produces the necessary equivalents for the reduction of the FePO$_4$ present in a digested sludge; this approach has been used to remobilize insoluble phosphate into a soluble form available for the struvite precipitation by dosing magnesium and ammonia [114]. Further, the remobilization of the insoluble FePO$_4$ salt, which constitutes the by-product of the phosphate removal in the wastewater treatment plant, is driven by the quantitative reduction of the Fe to Fe$^{3+}$, promoting the PO$_4$ remobilisation in the liquid phase. During the two-chamber operation, the pH increased up to 9 in the abiotic cathode thanks to the use of the protons in the cathodic reactions (i.e. iron and oxygen reduction); this promoted the production of the base that remained in the catholyte, as alkali cations (M$^{n+}$), instead of protons migrated into the cathode. The consequent alkalinisation resulted in an additional phosphorous remobilization due to the slightly alkaline pH. The MFC concept was shifted to a MEC concept (Fig. 5-A).
through the application of an external potential to increase the alkalinity production and the phosphorous remobilization from sewage sludge [118]. This study showed how the alkanisation of the cathodic chamber of a MEC, sustained by the anodic COD oxidation, can be successfully adopted as a strategy for the phosphorous remobilization thanks to the stimulation of a new mechanisms that involves a strong alkaline pH.

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

By applying voltages between 0.2 and 6.0 V, a strong chemical base is generated thanks to the partial exploitation of the chemical energy contained in the anodic substrates. The study conducted by the use of a MEC resulted in a significantly faster phosphate remobilisation from iron phosphate with respect to the use of a MFC. Indeed, the use of a MFC involves the electrochemical reduction of the FePO$_4$ and an oxygen reduction mechanism that generates the alkalinity, while by using a MEC, the strong alkanisation of the catholyte favours a substitution mechanism, in which the phosphate is remobilized and Fe(OH)$_n$ is precipitated. Moreover, the second remobilization mechanism offered an additional
advantage in the case of the presence of heavy metals in soluble form that are precipitated as insoluble hydroxides. A scaled-up reactor (Fig. 5-B), operated both under MFC and MEC conditions [119], further confirmed the increase of the phosphate remobilization through the application of an additional voltage due to the pH rise in the cathodic chamber. The study performed the kinetic analysis of the fluid particle: while in the MFC configuration the remobilization was performed by the diffusion in the liquid film around the sewage sludge particle, in the MEC the reaction resistance moved inside the sewage sludge particle.

### 2.5 Water sanitation and softening: alkali production, sulphide control and H₂O₂ disinfection

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

Rabaey and co-workers investigated the possibility of producing caustic during wastewater treatment using a three-electrode configuration and operating in electrolysis mode. The BES, equipped with a lamellar configuration, was operating at 1.77 V (1015 Am⁻³ volume of the anodic chamber) to supply high amounts of electron donor from acetate [120]. In these conditions, about 1.05 A was generated by the system, and up to 3.4 wt% caustic production has been reached, at an acetate to caustic efficiency of 61%. Subsequently, a direct effluent
from a brewery process was used and currents of up to 0.38 A within a six-week operational period were obtained.

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

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

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

Even if in this study the role of the microorganisms supporting the electricity generation has not been considered, the catholyte alkalinity generation resulted in an interesting application.
The sulphide was removed with an efficiency of 95.4 ± 4.4%, reached applying a low voltage. This setup successfully increased the sewage pH, avoiding the disadvantages linked to the standard iron salt dosing and the use of chemicals for the sulphide precipitation. Moreover, considering that higher pH shifted the equilibrium from volatile sulphide to non-volatile sulphide, lower residual sulphide emission to the sewer atmosphere can be obtained [128].

Hydrogen peroxide (H$_2$O$_2$) is a chemical compound characterized by a strong oxidation power exploited in several industrial applications (pulp and paper bleaching, synthesis of chemical, and textile bleaching). Generally, the H$_2$O$_2$ is produced through anthraquinone oxidation process or electrochemically approaches, which require significant energy inputs [129, 130]. An alternative production method is represented by a MEC, where the oxidation of wastewater organics at the anode is coupled to production of H$_2$O$_2$ at the cathode. For this process, no expensive catalysts are needed as carbon materials have been already tested for this reaction. An efficient production of H$_2$O$_2$ has been obtained in a MEC by applying a voltage of 0.5 V; around 1.9 ± 0.2 kg H$_2$O$_2$/m$^3$/day have been produced at concentration of 0.13 ± 0.01 wt% and an overall efficiency of 83.1 ± 4.8%. If a H$_2$O$_2$ concentration of 2–3 wt% can reached, the process can lead to several industrial implications [131]. Even if the H$_2$O$_2$ production it is not linked to an alkaline pH, during the experimental runs, the pH of the cathode increased from 7.2 ± 0.6 to 11.9 ± 0.5 after two hours and it remained around 12 during the remainder of the experiments. The alkalization of the catholyte resulted in an ion migration; the concomitant presence of a strong alkaline pH represents a favourable condition for the advance oxidation of recalcitrant compounds.
Table 1. Different bioelectrochemical processes in which the pH split is exploited

<table>
<thead>
<tr>
<th>Application</th>
<th>BES device</th>
<th>IEM</th>
<th>pH split utilization</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate extraction and concentration</td>
<td>MEC</td>
<td>AEM/BPM</td>
<td>Anode/extraction chamber acidification</td>
<td>[57, 58, 73]</td>
</tr>
<tr>
<td>Solventogenesis and acetogenesis control</td>
<td>MEC</td>
<td>AEM/CEM</td>
<td>Anode chamber acidification</td>
<td>[61]</td>
</tr>
<tr>
<td>CO₂ removal - biogas upgrading</td>
<td>MEC</td>
<td>AEM/CEM/BPM</td>
<td>Cathodic alkalization</td>
<td>[80, 81, 88]</td>
</tr>
<tr>
<td>Ammonium recovery and concentration</td>
<td>MFC/MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[87, 101, 132, 133]</td>
</tr>
<tr>
<td>Ammonia stripping</td>
<td>MFC/MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[102, 103, 108]</td>
</tr>
<tr>
<td>Phosphorous recovery and remobilization</td>
<td>MFC/MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[114, 115, 118, 119]</td>
</tr>
<tr>
<td>Alkali production</td>
<td>MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[120]</td>
</tr>
<tr>
<td>Water softening</td>
<td>MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[98, 121, 123]</td>
</tr>
<tr>
<td>H₂S control in sewer</td>
<td>MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[127, 134]</td>
</tr>
<tr>
<td>Water sanitation</td>
<td>MEC</td>
<td>CEM</td>
<td>Cathodic alkalization</td>
<td>[131]</td>
</tr>
</tbody>
</table>
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.
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