



Review

Bioelectrochemical ammonium recovery from wastewater: A review

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ABSTRACT

Due to the anticipated rise in demand for ammonia, the search for viable methods for its recovery has intensified in recent years, as traditional ammonia production is a high energy intensive process. Bioelectrochemical systems (BESs) offer an alternative solution for ammonia recovery since they have shown lower energy demand (in terms of $\text{kJ g}^{-1}\text{N}$ recovered) at lab-scale than other methodologies. In BESs, the bioelectrochemically generated current drives the transport of NH_4^+ from the wastewater to a concentration chamber through a cation exchange membrane before its subsequent recovery. This paper describes the fundamentals and opportunities for bioelectrochemical ammonia recovery (either by stripping, absorption, or precipitation) in different BES devices such as microbial fuel cells, microbial electrolysis cells, microbial desalination cells and bioelectroconcentration cells and compares the performance of all the reported experimental works so far. Moreover, the most critical challenges (low current density, nature and quantity of the carbon source, inlet ammonium concentration, use of membranes, energy yield and recovery efficiency) have been detailed and discussed in view of better understanding the current bottlenecks for its scale-up and, thus, for its prompt industrial adoption.

1. Introduction

The fundamental transformation of wastewater treatment towards a circular economy scenario creates a demand for efficient recovery of energy and nutrients such as nitrogen and phosphorus. Ammoniacal nitrogen in water causes eutrophication and is toxic in its non-ionized form (ammonia, NH_3). The combined costs related to its removal, health issues and climate change impact could amount to a total of €320 billion/y [1]. Ammoniacal nitrogen is paradigmatic, since its recovery is promising from both an energetic and material point of view. First, ammonia-based fertilizers increase crop yields and ensure efficient food production. In the context of global population growth, the demand for fertilizers is also expected to grow. Nowadays, most of the NH_3 is still produced through the energy-intensive Haber-Bosch process that uses harsh conditions. High temperature (typically 400–650 °C) and pressure (100–400 bar) are required to activate the reaction between hydrogen and nitrogen to produce NH_3 in the presence of an iron catalyst, enabling it to occur at a rate that is economical for its industrial production [2]. In 2020, NH_3 production reached 235 million tones and accounted for 8.6 EJ ($8.6 \cdot 10^{18}$ J) of energy consumption, equivalent to 2% of the total energy consumed globally [2,3]. On the other hand, NH_3 has recently

been appointed as a zero-carbon molecule that can provide the required energy storage medium for renewable sources [4]. NH_3 can be stored under mild temperature and pressure conditions, similarly to other current commercial fuels; it is easier to liquefy than hydrogen, the costs for its transportation and storage are lower, and liquid NH_3 has a greater volumetric hydrogen density than liquid hydrogen itself [5,6]. NH_3 already has a market of nearly 200 million tons/yr, making it the second most commercialized chemical in the world. Therefore, infrastructure at every scale is available for immediate implementation of an “ NH_3 economy”.

In urban and industrial wastewater, inorganic nitrogen appears mainly in two forms, NH_3 and NH_4^+ , the sum of which constitutes total ammoniacal nitrogen (TAN). The different approaches used to remove and recover TAN from wastewater can be classified into chemical, physical and biological processes. TAN can be removed chemically e.g. via chlorination [7], electrochemical oxidation [8] and photoelectrocatalysis [9]. Struvite precipitation has also been proposed for nitrogen removal and recovery [10], since it has an added-value as a slow-release fertilizer. However, its technoeconomic feasibility is often limited by the high reagent costs due to the unbalanced presence of required ions (NH_4^+ , PO_4^{3-} and Mg^{2+}) in the wastewater.

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The physical processes for nitrogen removal include ammonia stripping [11], reverse osmosis [12], ion exchange [13], electrodialysis [14] and the treatment using gas-permeable membranes [15,16]. These physical processes allow efficient ammonia recovery but are resource and energy intensive. For instance, the optimum boiling point for NH_3 stripping in the case of vacuum thermal stripping has been determined to be 65 °C at 25.1 kPa, and the liquid needs to be adjusted to a pH of 9.23 to stripping out more than 95% [17].

Biological removal methods are sustainable and allow TAN removal with lower capital and operational costs than physical or chemical methods. The main biological processes for TAN removal include nitrification–denitrification [18], nitrification/denitrification or shortcut nitrogen removal [19], and partial nitrification [20] plus anammox [21,22]. Finally, the use of bioelectrochemical systems (BES) [23,24] allows TAN removal and recovery without high energy demand or dosage of chemicals to reach a favorable pH.

BES are biologically-catalyzed electrochemical systems that contain two connected electrodes (an anode and a cathode). BESs have gained importance in the fields of bioenergy and biorefinery as they can employ microorganisms as biocatalysts and use solid electrodes in electrochemical cells to supply or extract electrons driving versatile biochemical reactions producing chemicals and fuels from CO_2 or consuming organic waste as carbon sources [25]. The biological catalysts are electroactive microorganisms capable of exchanging (i.e. transfer or uptake) electrons with a solid electrode. For instance, exoelectrogenic microorganisms (i.e., those able to transfer electrons extracellularly to a solid anode) act as biocatalysts in the oxidation of readily biodegradable organic compounds. The electrons released in the oxidation travel

through an external circuit and are received by the cathode. At the cathode, a reduction reaction occurs (usually a chemical reaction), and the electrons are donated to a terminal electron acceptor.

BESs used for TAN recovery can be divided into four categories based on their operating principle (Fig. 1). If the oxidation and reduction reactions result in a negative Gibbs energy variation, the flow of electrons becomes spontaneous and electrical energy is produced. This system is called Microbial Fuel Cell (MFC). Oxygen is the most used cathodic electron acceptor in MFCs due to its high reduction potential and availability.

In Microbial Electrolysis Cells (MECs), the occurring semi-reactions lead to a positive Gibbs energy variation and hence an external energy is required to drive the oxidation and reduction reactions. The application of external energy allows the boosting of the electric current and enables e.g. the generation of hydrogen at the cathode. Therefore, some of the external energy applied can be recovered as hydrogen.

Similarly to MFCs, in microbial desalination cells (MDCs) the current generation is spontaneous. In these systems, a third desalination chamber placed between the anodic and cathodic chambers, which is separated from them with a pair of ion exchange membranes (IEMs), usually with a cation exchange membrane (CEM) facing the cathode side and an anion exchange membrane (AEM) facing the anode side. The electric potential gradient created by the electroactive bacteria drives ion transport through these membranes.

Bioelectroconcentration cells (BECs) also incorporate a third chamber separated with IEMs and the electric field drives charged species through these ion-selective membranes, but in contrast to MDCs, in BECs external energy is applied and the ions are concentrated in the middle

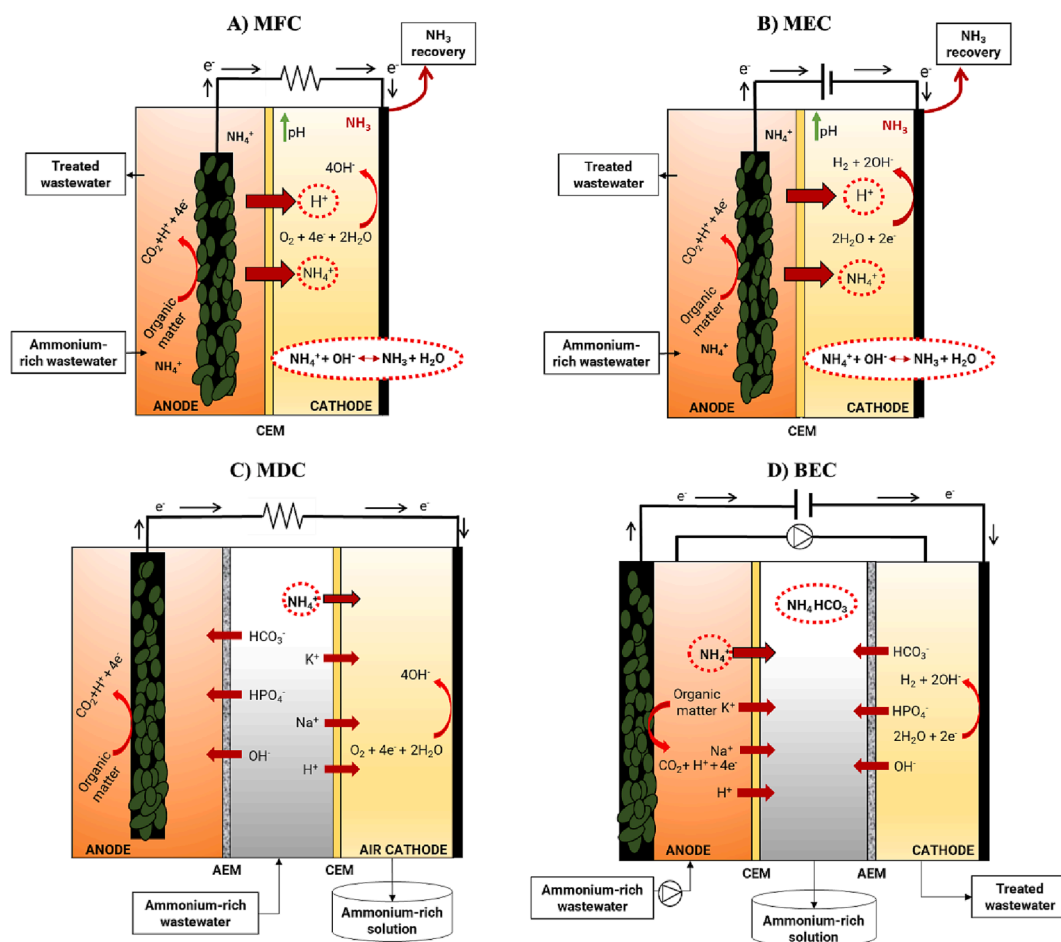


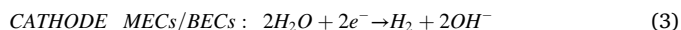
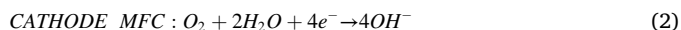
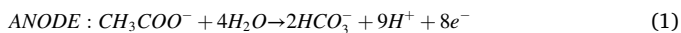
Fig. 1. Different bioelectrochemical systems for ammonium recovery: A) Microbial Fuel Cell; B) Microbial Electrolysis Cell; C) Microbial Desalination Cell, and D) Bioelectroconcentration cell.

chamber [26,27].

In BESs, the energy stored in the biodegradable organic contaminants of wastewaters can be converted into electrical energy that can drive the transport of TAN, with simultaneous production of other valuable resources such as electricity or hydrogen [28,29]. Moreover, the process can run with minimal dosage of chemicals for pH control [30]. The combination of both factors allows for more energy-efficient TAN recovery compared to conventional recovery methods [29]. Since previous reviews focusing on bioelectrochemical TAN removal and recovery were published [31–33] advances have been made with the reactor configurations, scaling up and recovery efficiencies and new challenges have been encountered. This review provides an overview of the current state of bioelectrochemical TAN recovery, and the fundamental mechanisms involved. Afterwards, the section Challenges and Perspectives describes the aspects that need to be addressed in this field to boost bioelectrochemical TAN recovery and proposes innovative guidelines for the design and operation of these systems.

2. Fundamentals of bioelectrochemical TAN recovery from wastewater

In BES, the anodic chamber usually receives a feed containing TAN and organic matter. Organic matter is oxidized and electrons are released (i.e., acetate oxidation, Eq. (1)) and transported through an external circuit to the cathode, where they are used for processes such as oxygen reduction in MFC (Eq. (2)) or hydrogen production in MECs or BECs (Eq. (3)).



The electron flow induces the transport of positively charged species (cations) across the CEM to maintain the charge neutrality [34]. Thus, this process, also known as electromigration, transports the NH_4^+ contained in the wastewater from the anodic to the cathodic chamber using

charge balance as the driving force. Anodic organic matter oxidation also releases protons that acidify the anolyte (Eq. (1)) whereas the cathodic chamber tends to become alkaline because of the cathodic hydroxyl-producing reduction reactions (Eqs. (2)–(3)). The pH gradient over the membrane is beneficial for TAN recovery since once NH_4^+ is transported to the cathode, it is partially displaced to NH_3 ($\text{pK}_a = 9.246$ at $T = 25^\circ\text{C}$) due to the high pH and the NH_4^+ concentration gradient is maintained. However, the pH gradient also increases anodic and cathodic overpotentials and decreases the system performance from an energetic point of view [36]. Thus, there are three fundamental steps for bioelectrochemical TAN recovery: 1) NH_4^+ transfer from anodic to cathodic chamber, 2) NH_4^+ displacement to NH_3 due to alkaline conditions and 3) NH_3 extraction for its recovery (Fig. 2).

2.1. NH_4^+ transfer from anodic to cathodic chamber

The first step is the transfer from the anodic to the cathodic chamber through the CEM. The CEM consists of dense crosslinked polymer chains fixed with negatively charged groups, which, due to the relatively small hydrated ionic size and fast diffusivity, allows NH_4^+ to be easily transported across it [35]. In this sense, Volkov et al [38] reported the hydrated radius for different cations, with NH_4^+ (0.331 nm) being similar to K^+ and smaller than other cations such as Na^+ (0.358 nm), Ca^{2+} (0.412 nm) or Mg^{2+} (0.430 nm). The main mechanisms driving the transportation of NH_4^+ through the CEM are: i) Donnan exclusion (the fixed negatively charged groups in CEMs create a Donnan potential across the membrane which prevents anion diffusion), ii) electromigration (ammonium ions are attracted towards the cathode due to the potential difference applied across the membrane), iii) concentration gradient (ammonium diffuses from a higher concentration chamber, i.e. the anode, to an area of lower concentration, i.e. the cathode, until equilibrium is reached), iv) ion exchange (CEM have mobile cations associated with the fixed negatively charged groups that can undergo ion exchange with ammonium ions enabling, thus, their diffusion through the membrane) and v) water-mediated transport (water molecules may form hydration shells around the ammonium ions, allowing them to cross the membrane via a solvation/desolvation process). The specific

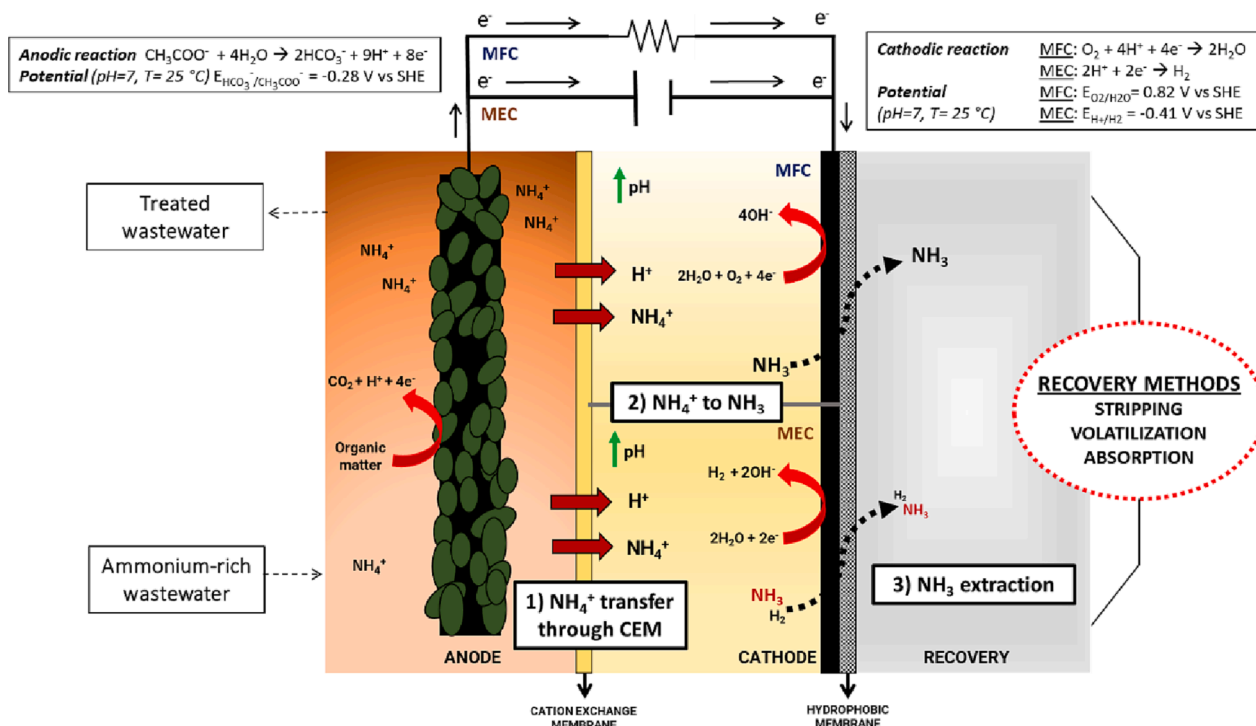


Fig. 2. Schematics of bioelectrochemical TAN recovery in BES.

mechanism occurring depends on factors such as ammonium concentration, membrane properties, pH (see section 2.2), temperature, and the presence of other ions in the solution and the efficiency of the NH_3 extraction from the catholyte [31,37].

Yang and Qin [35] reviewed the applicability of widely used commercial CEMs for TAN recovery (i.e. Nafion N117, CMI-7000, CMH-PP Ralex, CEM Type I and II). However, the link between NH_4^+ transport and current density is not fully understood yet. While some studies indicate that NH_4^+ transport dominates the current across the CEM and one NH_4^+ ion is transported per each electron passing through the external circuit [39], other studies suggest that NH_4^+ ions may transport only 40% of the total current [40]. Na^+ , K^+ , Mg^{2+} , Ca^{2+} , or NH_4^+ are the cations that are most frequently transported, based on their concentration. So, the presence of cations other than NH_4^+ in a high concentration can hinder TAN recovery [40]. This competition can be quantified through the transport number (Eq. (4)), a dimensionless parameter used to directly describe the number of ions that move across the membrane. The transport number of an ion species i is defined as the proportion of the charge transported by i with respect to the total charge transported [41,42].

$$t_i = V \cdot F \cdot z_i \cdot \frac{c_i(0) - c_i(t)}{\int_0^t I_{\text{tot}} dt} \quad (4)$$

where t_i represents the transport number of i , V is the volume of the catholyte, F is the Faraday constant, z_i is the charge carried by ion i , $c_i(0)$ and $c_i(t)$ are the concentrations at time of zero and time of t , respectively, and $\int_0^t I_{\text{tot}} dt$ is the sum of the charge transferred by the electrons at the external circuit within the time period t . Ideally, bioelectrochemical TAN recovery systems should aim at a NH_4^+ transport number close to one [35].

Furthermore, since the migration of the ions is current driven, it is important to consider the ratio between current and TAN loading rate. The load ratio (L_N) [43], is the ratio of the electrical current generated from the fed wastewater over NH_4^+ loading [28,44] (Eq. (6)).

$$L_N = \frac{i \cdot M_{\text{TAN}}}{Q_{\text{TAN}} \cdot z_{\text{NH}_4^+} \cdot F} \quad (6)$$

where i is the electrical current generated (A), M_{TAN} the molar mass of TAN (14 gN/mol_{TAN}), Q_{TAN} the TAN loading into the receiving compartment in g_{TAN}·d⁻¹, $z_{\text{NH}_4^+}$ the charge of NH_4^+ being 1, and F the Faraday constant (96485 C mol⁻¹). A L_N lower than 1 means that the current is too low to transport all the TAN and, thus, TAN will accumulate in the anodic chamber. A L_N equal to 1 describes a situation where the TAN loading and the applied current are balanced. Finally, L_N values higher than 1 mean that all the TAN and additional cations could be transported by the current produced.

2.2. NH_4^+ transformation to NH_3

Ammonium is a weak acid ($\text{pK}_a = 9.246$ at 25 °C) and thus partially dissociates in aqueous solution. The relative amounts of NH_4^+ and NH_3 are determined by the pH of the medium. Therefore, a pH higher than the pK_a is necessary to drive NH_4^+ displacement to NH_3 [45,46]. According to Le Chatelier's law, a continuous NH_3 extraction would boost NH_4^+ displacement to NH_3 , which would in turn favor NH_4^+ transfer through the CEM due to a higher concentration gradient. Hence, most of studies aim at an electrochemically driven pH that is significantly higher than the pK_a of NH_4^+ . If the applied current enables a faradaic production of hydroxyls in the cathode (Eqs. (2) and (3)), the pH along the electrode surface can be calculated as a function of the applied current density, and the diffusion of H^+ and OH^- . For example, the pH along the cathode at 30 μm from the surface was calculated as 13.8 for current densities of approximately 17 A m⁻² (under certain operational conditions) [37]. Liu et al [40] demonstrated that the pH can be regulated (i.e. it can reach

lower values) when NH_4^+ ions are transported across the CEM due to their reaction with hydroxyls.

2.3. NH_3 extraction for its recovery

Efficient NH_3 extraction can boost the performance of the cathodic equilibrium-based steps and, thus, TAN recovery. The more common techniques for NH_3 extraction are stripping, transmembrane chemisorption (TMCS) and forward osmosis [29]. An emergent alternative is the integration of an electrode to a hydrophobic membrane forming a gas diffusion electrode (GDE). Then, TAN can be recovered on the other side of the membrane as a dissolved salt with an additional recovery chamber containing an acidic solution. Afterwards, NH_3 can be recovered either using acidic absorption, concentration, or precipitation.

Stripping is achieved by sparging a gas through the TAN-concentrated solution. High performance requires high gas flow rates, elevated temperature and high pH and, thus, considerable energy input (30–90 kJ gN⁻¹) in addition to the need for base dosage for pH adjustment [29,47]. Therefore, the integration of a hydrophobic membrane with gas-permeable microporous (i.e., PTFE- or PP-based membranes) has gained attention to decrease the energy requirements. The driving force for TAN recovery is the ammonia concentration gradient across the membrane, which is promoted by the pH difference between the catholyte and the solution in the recovery chamber. The least used methodology in BES is forward osmosis, which is based on the application of an osmotic pressure through a semipermeable membrane to separate water from dissolved ammonium.

3. TAN recovery using MFCs

TAN removal from wastewater has been studied using MFCs [45,48,49]. NH_4^+ oxidation linked to electricity generation has been already reported at lab scale [50]. However, this review focuses on TAN recovery, which has been under explored. Table 1 summarizes all the research conducted on TAN recovery using MFCs. This technology is still emerging and most experiments have been conducted at lab-scale and more than 80 % have used synthetic wastewater mimicking urine, pig slurry or digestate. The electrical energy output, the lack of need for chemicals and the low energy requirements (no voltage applied) makes MFCs interesting for TAN recovery. However, the low solubility of oxygen in water can limit its availability for electrochemical reduction when an external stripping unit is used. To avoid this limitation, air diffusion cathodes where oxygen diffuses through the cathode electrode have been used [51]. There is no difference in the materials utilized for TAN recovery in MFCs (Fig. 1A) compared to those employed in other types of MFCs. The most common anodic materials are carbon felt and graphite felt due to their high conductivity, mechanical stability, relatively low cost, surface area and porosity for providing abundant redox reaction sites [52,53]. Cathodic materials are diverse, Pt being the most used catalyst for the reduction reaction and stainless steel the alternative cheaper solution.

Regarding the configuration, more than 90% of the MFC-based TAN recovery studies use double-chamber configuration and the current drives the NH_4^+ migration from the anode chamber to the cathode chamber through the CEM. Taking advantage of the high cathodic pH and of the air inlet (in an MFC, oxygen reduction is the targeted cathodic reaction), TAN is recovered by stripping, volatilization or by recirculating the highly N-loaded catholyte through an absorption column [47,50]. The best results in double-chamber systems are those reported by Kuntke et al. [54], that achieved a TAN recovery rate (TAN RR) of 9.57 gN m⁻² d⁻¹ at a current density of 2.6 A m⁻² using undiluted urine. They also reported an energy net yield for ammonia recovery of -10 kJ gN⁻¹ and, resulting in a net energy yield of -2.8 kJ gN⁻¹. This result highlights the advantages of the MFC facilitated TAN recovery over the conventional NH_3 stripping that used around 32 kJ gN⁻¹ [55]. The more recent reports on double-chamber MFCs have not led to higher TAN RRs.

Table 1
Summary of the experimental reports on bioelectrochemical TAN recovery using MFCs.

Configuration/ Chambers	Influent Type	TAN [g L ⁻¹]	Electrode materials		Recovery Methodology	Product	Power density [W m ⁻²]	Current density [A m ⁻²]	TAN RE [%]	TAN RR [gN m ⁻² d ⁻¹]	Energy consumption (+) or production (-) [kJ gN ⁻¹]	Reference
			Anode	Cathode								
Single	Human urine	1.12	Carbon felt	Pt coated carbon paper	Precipitation	Struvite	0.36 ^b	0.97 ^a	71.1	15.1 ^a	n.r.	[58]
Double	Synthetic urine	4	Graphite felt	Pt coated Ti felt	Volatilization + Absorption	Ammonium sulfate	0.22	0.50 ^b	25.37 ^a	3.3b	-3.46	[34]
Double	Real urine	4	Graphite felt	Pt coated Ti felt	Stripping + Absorption	Ammonium sulfate	0.67	2.6	73.94	9.57	-10	[54]
Double	Pig slurry	2.50	Carbon felt mesh	Stainless steel mesh	Stripping + Absorption	Ammonium sulfate	0.05	0.15	38.4	n.r.	n.r.	[62]
Double	Synthetic domestic	0.04	Graphite felt	Carbon fiber brush	Volatilization	Ammonia	0.23	0.02	n.r.	0.9	n.r.	[63]
Double	Reject and digestate	1.01	Carbon brush	Pt coated stainless steel mesh	Microbial production	Microbial protein	0.10	0.07	60.5	6.8	154.8 kJ m ⁻³	[56]
Triple	Synthetic	1.78	Carbon felt	Pt coated carbon fibers	Stripping + Absorption	Ammonium sulfate	n.r.	0.05	53.6	12.7	111.6 kJ m ⁻³	[51]
Double	Urine	0.44	Stainless steel mesh	Stainless steel mesh	Precipitation	Struvite	0.01	0.02	46.0	n.r.	n.r.	[59]
Double	Synthetic	0.45	Carbon brush	Carbon brush	Stripping	Ammonium sulfate	0.10	1.20	90.8	6.9	n.r.	[50]
Double	Synthetic urine	0.60	Carbon brush	Pt coated carbon cloth	Stripping + Absorption	Ammonium sulfate	0.06	0.42	91.6	2.7	n.r.	[57]

^a calculated, ^b maximum value obtained, n.r. = not reported.

Yang et al. [56] reported an integration of MFC and TAN recovery as N-source for microbial protein production. This two-step process reached recovery efficiency values up to 53–61% (at initial concentrations around 2 g/L) depending on the initial ammonium content of the wastes. Zhang et al. [50] reported a TAN recovery efficiency (TAN RE) of 90.8% with a TAN RR of 6.9 gN m⁻² d⁻¹ at a current density of 1.2 A m⁻² with the use of a soluble electron mediator in the catholyte. Han et al. [57] reported a high TAN RE (91%) at a current of 0.416 A m⁻² and a TAN RR of 2.6 gN m⁻² d⁻¹. Similarly, Losantos et al. [51] reported a triple-chamber MFC set-up where the cathode chamber was delimited by an air diffusion cathode setup which allowed an airflow to be forced through the cathode surface, providing oxygen while simultaneously enabling ammonia stripping. This system had a TAN RE of 31.2 % with a TAN RR of 6.8 gN m⁻² d⁻¹ at a current density of 1.6 A m⁻².

On the other hand, fewer studies reported the use of single-chamber MFCs for TAN recovery. Besides volatilization/stripping [34,54] or absorption, precipitation in a single-chamber MFC has been proposed [58]. For instance, struvite (MgNH₄PO₄) precipitation has shown successful results at lab-scale: TAN RE around 50% in addition to the possibility of recovering other nutrients, such as phosphorus [59,60]. Zang et al. [58] reached current densities close to 1 A m⁻² with TAN RE higher than 70% and TAN RR ≥ 10 gN m⁻² d⁻¹ at initial concentrations greater than 1 g/L when coupling a struvite precipitation reactor with a single-chamber MFC [58]. The major drawback of these systems is that, in general, there is an imbalance between phosphorus and nitrogen, which leads to low N recovery. To avoid this problem, the addition of P-rich material has been proposed [61].

4. TAN recovery using MECs

The switch from an MFC to an MEC for TAN recovery changes the perspective in terms of energy consumption. In MECs (Fig. 1B), external electrical energy is applied to run the current-generating oxidation and reduction reactions and, despite this increased energy demand, MECs have several advantages: 1) higher current densities can be achieved, which increases electromigration, 2) higher catholyte pH values, promoted by alkalinity generation during the reduction reaction (Eq. (3)), stimulate the transformation of NH₄⁺ in NH₃, 3) hydrogen production can assist in stripping NH₃ from the catholyte and maintaining a concentration gradient over the CEM and 4) the produced hydrogen gas holds a higher economic value than electricity.

Table 2 summarizes the performance of the MECs for TAN recovery (current density, TAN RR and TAN RE). While MECs often aim at hydrogen production, in some of the reports from Table 2, the cell is operated as an MEC (i.e., energy is applied) to boost current density despite the cathodic reaction is mainly oxygen reduction. The two most usual configurations used in MEC-based TAN recovery are double-chamber MECs and triple-chamber MECs. TAN has been also recovered in single chamber MECs by precipitation as struvite [64], but most of the studies aiming at struvite precipitation have focused on P recovery optimization instead of TAN recovery [65,66] due to the stoichiometric excess of N in real wastewaters.

In double-chamber MECs, NH₃ is usually extracted from the catholyte via stripping using the air inlet or the produced gas, and then recovered in a separate acidic absorption column. Either the cathodic chamber can be aerated [40] or the catholyte can be aerated in a separate stripping column [67]. The oxygen from air can serve as the cathodic electron acceptor allowing operation with high cathode potential that leads to low external energy demand. Stripping, however, is energy intensive as an important amount of gas needs to be sparged through the catholyte solution. Qin et al. [68] concluded that more than 50% of the total energy consumed was for active aeration in their tubular double-chamber MEC. While TAN removal rates have been reported to increase up to 173 gN m⁻² d⁻¹ [24], the highest TAN RR reported in MEC has been 70 gN m⁻² d⁻¹ obtained by Carucci et al. [69] in a double-chamber MEC with TAN recovered via stripping and

Table 2
Summary of the experimental reports on bioelectrochemical TAN recovery using MECs.

Configuration/ Chambers	Influent		Electrode materials		Recovery		Current density [A m ⁻²]	TAN RE [%]	TAN RR [gN m ⁻² d ⁻¹]	Energy consumption [kJ gN ⁻¹]	Hydrogen production [m ³ H ₂ m ⁻³ d ⁻¹]	Reference
	Type	TAN [g L ⁻¹]	Anode	Cathode	Methodology	Product						
Double	Synthetic	1	Carbon felt	Steel wire	Stripping + Absorption	Ammonium chloride	1.6	94.0	45.9	35.6	2.48	[73]
Triple	Synthetic	1	Carbon felt	Air diffusion electrode	Stripping + Absorption	Ammonium nitrate	2.5	45.3	9.6	7.92	n.p.	[51]
Double	Diluted urine	0.70	Graphite felt	Platinum	Stripping + Absorption	Ammonium borate complex	23.1	n.r.	n.r.	n.r.	48.6	[24]
Double	Pig slurry	2.12	Carbon felt mesh	Stainless steel mesh	Stripping + Absorption	Ammonium sulfate	0.06	94.3	24 ^a	n.r.	n.p.	[62]
Double	Synthetic	5.1	Carbon felt	Stainless steel mesh	Stripping + Absorption	Ammonium sulfate	27	n.r.	n.r.	21.7	n.r.	[67]
Double	Synthetic	0.39	Carbon brush	Pt/C coated carbon cloth	Stripping + Absorption	Ammonium sulfate	1.89 ^b	66.2	10.2	n.r.	n.p.	[40]
Triple	Digestate	1.9	Carbon felt	Stainless steel mesh	TMCS	Ammonium sulfate	1.4	89	66	n.r.	n.r.	[72]
Double	Digestate	1.9	Carbon felt	Stainless steel mesh	TMCS	Ammonium sulfate	0.61	n.r.	16.8	n.r.	n.r.	
Double	Effluent of MAP reactor	3.40	Ti plate with MMO coating	Ti plate with MMO coating	TMCS	Ammonium sulfate	1.7	31	n.r.	1.4	n.r.	[74]
Double	Synthetic	0.78	Carbon brush	Pt/C coated carbon cloth	Stripping + Absorption	Ammonium sulfate	1	83	7.1	16.2	n.p.	[75]
Double	Synthetic	1	Granular graphite	Granular graphite	Concentration	Ammonium in catholyte	19 A m ⁻³	92	10.38	8.3	n.p.	[76]
Double	Synthetic	0.78	Carbon brush	A/C coated Carbon cloth	Stripping + Absorption	Ammonium sulfate	0.01 A ^b	90.1	n.r.	4.68	n.r.	[68]
Double	Digestate	1.50	Carbon felt	Granular graphite	TMCS	Ammonium sulfate	3.6	n.r.	6.72	18	n.p.	[77]
Triple	Synthetic	1	Carbon brush	Ni-based GDE	TMCS	Ammonium sulfate	25.5	n.r.	36.2	5.79	0.2	[16]
Double	Synthetic	2.50	Graphite felt	Stainless steel mesh	Stripping + Absorption	Ammonium sulfate	9.4 ^b	n.r.	70	12.9	n.p.	[69]
Single	Synthetic	0.06	Graphite brush	Stainless steel mesh	Precipitation	Struvite	12	n.r.	n.r.	n.r.	2.3	[64]
Triple	Mineral Medium	0.09	Granular graphite	Granular graphite	Concentration	Ammonium sulfate	145 mA	n.r.	n.r.	n.d	n.r.	[78]
Triple	Synthetic dark fermentation	0.03	Granular graphite	Granular graphite	Concentration	Ammonium concentrate	300 mA	81.0	0.7 gN d ⁻¹	98.85	n.r.	[79]
Five	Synthetic	20 mM	Graphite fiber brush	Stainless steel mesh	Concentration	Ammonium sulfate	1.9 mA	68	0.47 gN L ⁻¹	10.44	n.r.	[80]

^a calculated, ^b maximum value obtained, n.r. = not reported, n.p. = not produced, A/C = Activated carbon, MMO = Mixed metal oxide, TMCS = Transmembrane chemiabsorption.

adsorption. Triple-chamber systems with membrane contactors have been studied as a less energy-intensive and simple alternative. In such systems, TAN is concentrated in a recovery chamber that is separated from the catholyte solution with a membrane. The recovery chamber needs to be separated in a way that allows efficient transfer of TAN from the cathodic chamber to the recovery chamber without this being the limiting step and without affecting the cell performance. Two possibilities arise: the use of hydrophobic membranes and the use of GDEs. In the first case, the small pore size and the hydrophobic nature of the membrane prevent the liquid phase from entering the pores due to the surface tension effect [70]. Gonzalez-Salgado et al. [71] reviewed the fundamentals and pilot- and full-scale applications of these membranes and concluded that the pre-treatment of the wastewater and the membrane fouling/wetting are the major challenges of this technology [71].

Cerrillo et al. [72] demonstrated that a triple chamber MEC with hydrophobic membrane (e.g. PTFE) produced twice as much current intensity than a double chamber MEC (1.40 A m^{-2} and 0.61 A m^{-2} , respectively). Similarly, TAN RR was significantly higher in triple chamber MECs ($36 \text{ gN m}^{-2} \text{ d}^{-1}$) than in double chamber ($17 \text{ gN m}^{-2} \text{ d}^{-1}$), mainly due to a higher cathodic pH in the former scenario [72]. Hou et al. [16] studied the use of a Ni-based GDE and obtained 40% higher TAN RR ($36.2 \pm 1.2 \text{ gN m}^{-2} \text{ d}^{-1}$) and higher current density (25.5 A m^{-2}) than what was obtained in a control reactor with separated electrode and hydrophobic membrane. Operation under applied external energy allows for increased current densities and thus the systems can be operated under high L_N even when using wastewater with high TAN concentration [16].

TAN recovery performance in MECs can be affected by factors limiting current generation (e.g., substrate composition, conductivity, pH, inhibiting compounds) or ion transfer (e.g., competing cations, solids/compounds causing membrane fouling). Most MEC studies have still been conducted using synthetic feed solutions due to the complex matrix of most real streams. Operation under applied voltage or current allows easy control of the system, as the amount of energy applied can be easily adjusted. However, due to the involvement of microorganisms, BES are more subject to current fluctuations than electrochemical systems, which also affects the TAN recovery due to the current-driven electromigration. There are three different strategies for applying external electrical energy: 1) controlling electrode potential (potentiostatic), 2) controlling cell voltage and 3) controlling the current (galvanostatic). The external applied voltage required depends on the desired oxidation and reduction reactions as well as on the internal resistance of the system. Values have ranged from 0.2 V with an oxygen reducing cathode [51] to above 2 V with a hydrogen producing cathode [67]. Importantly, poor performance on one electrode may cause the other electrode potential to change accordingly, which could bring it out of the range required for the desired oxidation or reduction reaction, thus limiting the current intensity generated.

In operation under constant current, electrode potentials can change rapidly due to a variety of factors (e.g., changes in substrate concentrations) and, in the case of BES, extreme electrode potentials can damage the electroactive biofilm. For example, a significant increase in the anode potential can bring the electrode potential into a range where oxidation of water to oxygen occurs in addition to the oxidation of organic matter. This oxygen evolution can decrease the coulombic efficiency, trigger the anodic biofilm detachment, and enhance the growth of undesired aerobic microbial cultures, thus hindering the utilization of the chemical energy of the organic matter.

Similarly to MFCs, carbon-based materials are the most common as anode electrodes in MECs. Cathode electrode materials, however, have varied as the external energy addition allows the realization of different cathodic reduction reactions. The most commonly used catalyst for oxygen reduction is Pt, while steel-based materials have been used for both oxygen reduction and hydrogen evolution as a cheaper alternative. Studies aiming at cathodic CO_2 reduction have been conducted with carbon-based cathodes (carbon granules).

5. TAN recovery using MDCs and BECs

MDCs generate electrical energy like MFCs, but a distinguishing feature is the incorporation of an additional chamber. In the conventional MDC configuration, the desalination chamber is placed between the anodic and cathodic chambers and is separated from the anodic chamber with an AEM and from the cathodic chamber with a CEM. The charge imbalance between the anolyte and the catholyte solution resulting from the current generated facilitates the transport of cations and anions through the CEM and AEM, respectively [81]. The introduction of additional membranes and chambers between the anode and the cathode increases the internal resistance of the system. However, the high concentration gradients between the anolyte and the desalination solution, as well as between the catholyte and the desalination solution, generate junction potentials over the membranes, which can assist in overcoming the potential losses created by the addition of the desalination chamber [82]. Furthermore, since in MDCs TAN is transferred from the desalination chamber to the cathodic chamber, anodic microorganisms are not exposed to high concentrations of TAN, which minimizes the risk of anodic inhibition by ammonia and enables TAN recovery from extremely concentrated water streams [83]. In fact, the current densities obtained in MDCs for TAN recovery have been generally one order of magnitude higher than what has been obtained in MFCs for TAN recovery.

In MDCs (Fig. 1C), TAN is usually recovered from the catholyte via stripping followed by absorption as the cathodic pH increases and the catholyte is aerated to provide oxygen as an electron acceptor. Yang et al. [84] switched the position of AEM and CEM and obtained TAN RR of $11.5 \text{ g m}^{-2} \text{ d}^{-2}$ while concentrating TAN from the anolyte to the middle chamber. In addition to the traditional triple-chamber configuration, TAN recovery has been studied with submersible double-chamber MDCs, in which TAN is recovered from the surrounding solution [83,85]. In such systems, the AEM and CEM membranes are placed outside the anodic and cathodic chambers and no additional inner chamber is needed. TAN RRs in such submersible MDCs have increased up to $86 \text{ gN m}^{-2} \text{ d}^{-1}$ [85]. The TAN RR reported in MDCs are the highest among those BESs that do not require applied potential.

A BEC (Fig. 1D) is a hybrid microbial electrolysis/electrodialysis cell specifically designed to recover TAN and other ions. Like conventional MDCs, BECs contain an additional chamber between the anodic and cathodic chambers, which is separated from the anodic chamber by a CEM and from the cathodic chamber by an AEM. External electrical energy is applied to generate current that drives the transport of TAN and other cations from the anolyte to the concentration chamber, while simultaneously transferring anions (e.g. PO_4^{3-} , HCO_3^-) from the cathodic chamber to the same concentration chamber. Due to the alternation of AEM and CEM, configurations with up to six chambers have been reported. The outlet of these configurations is a TAN-concentrated solution and a TAN-free solution. The use of external energy allows the operation at high current densities, which in turn makes it possible to reach high TAN RRs. The highest TAN RR in BESs reported so far was reached by Ledezma et al. [27], who reported an RR of $430 \text{ gN m}^{-2} \text{ d}^{-1}$ obtained in BEC with 50 A m^{-2} . They demonstrated the recovery of a nitrogen-rich solid from synthetic urine (in the form of pure ammonium bicarbonate crystals with 17 % N content) without any chemical addition. The use of external energy, however, increases the energy consumption of the system.

Undesired diffusion of TAN (as NH_3) through the AEM has been reported in both MDCs and BECs [27,86]. Such diffusion can not only decrease the TAN RE, but also lead to inhibition of the anodic biofilm by free ammonia. This transport usually results from the high concentration gradient over the membrane and insufficient permselectivity of the membranes [27,87]. TAN can be transported through the AEM via facilitated diffusion in which a part of the NH_4^+ is converted to NH_3 due to the high pH value inside the AEM. The NH_3 then diffuses through the AEM and is converted back to NH_4^+ upon entering the acidic solution

[87]. The transport of desired ions and the prevention of the transport of undesired ions can be enhanced by using selective membranes that only allow the transport of specific ions. The use of selective CEMs can significantly increase the RE of TAN recovery from wastewaters that often contain multiple cations [88]. Membranes are also susceptible to fouling over time, so it is desirable to use membranes with better anti-fouling characteristics.

6. Challenges and perspectives

6.1. Current density: Electrochemical systems vs bioelectrochemical systems

NH_4^+ transport through the CEM, i.e. electromigration, is driven by current and, thus, high current densities result in high TAN RRs. In MFCs and MDCs, the current is generated spontaneously, but in MECs and BECs, external energy is applied and significantly higher current densities (and, thus, higher TAN RRs) have been obtained (Fig. 3A) at the expense of lower energy yield. Moreover, high current densities result in a higher catholyte pH, which favors TAN recovery. In a different scenario, migration of other cations from the cathode to the anode has also been used to improve TAN recovery. The Donnan dialysis, which means the exchange of ions of the same charge through a membrane, will take place when there is a concentration gradient over the membrane [96]. If there is no current intensity, then cations other than NH_4^+ that have accumulated on the catholyte side may move back to the anolyte side if a positively charged ion moves simultaneously from the anolyte to the catholyte. During TAN recovery, it is possible to utilize the accumulated K^+ and Na^+ cations to facilitate the transport of NH_4^+ from the anolyte to the catholyte, provided that most NH_3 has been effectively removed from the catholyte.

Thus, bioelectrochemical TAN recovery needs high current densities. For instance, the highest current densities reported so far are 37.6 A m^{-2} (average of 29.3 A m^{-2}) applying 1.46 V by Ledezma et al. [27] in a BEC. This reactor was operating with synthetic urine (pH 9.2) and adapted biomass. CE was 94.43%, meaning that the BECs transformed most of the chemical energy of the COD into electric charge. It has been reported that high anodic pH results in high CE and high current densities since microbial diversity is lower due to the more restrictive conditions and, thus, exoelectrogens face less competition for substrate [97].

In any case, current densities obtained using BES are still much lower than those reported for purely electrochemical systems (Fig. 3B). TAN RRs in electrochemical separation processes are usually $120\text{--}1010 \text{ gN m}^{-2} \text{ d}^{-1}$ across membranes with high selectivity (greater than 90%)

from synthetic solutions [47,98,99]. Most of electrochemical-based TAN recovery studies have a physical separation between the cathode and the hydrophobic membrane, which can limit the diffusion of gaseous NH_3 [100]. For instance, high TAN transport rates have been reported in a purely electrochemical system such as $335 \text{ gN m}^{-2} \text{ d}^{-1}$ at a current density of 50 A m^{-2} and an energy demand of 56.3 kJ gN^{-1} [98]. Lee et al. [101] reported a novel electrochemical approach using GDEs with a TAN RR of $890 \text{ gN m}^{-2} \text{ d}^{-1}$ with synthetic livestock wastewater at a current density of 100 A m^{-2} and a TAN RE close to 100%. As observed, the current produced in BES is at much lower than that produced in electrochemical systems but, in return, BESs consume less energy and can use the electrons from a waste (wastewater treatment) rather than from a conventional anodic oxidation reaction.

The higher energy requirements of electrochemical systems are their main drawback, whereas the lower current densities are the main shortcoming of BESs. In fact, the low amount of energy required per gram of N recovered currently justifies the present focus on BES. Beckinghausen et al. [61] reviewed the current research regarding nitrogen recovery and reported that MDC had the lowest ratio of the energy input vs the energy output: 0.1. The authors mentioned that BES, membrane technologies, and stripping appear to be the best options for recovering TAN from reject water from digestate balancing energy requirements and efficiency [61]. Therefore, further research should focus on increasing current densities without a substantial rise in energy requirement. Even though external energy is required in MECs and BECs, the energy demand remains comparable to that of many other conventional nitrogen removal processes (note that TAN removal is less beneficial than TAN recovery from a circular economy point of view). Several MEC studies have reported energy consumption of less than 21.6 kJ gN^{-1} , which is in the same range as nitrification/denitrification (46.8 kJ gN^{-1}), air stripping (32.4 kJ gN^{-1}) and anammox (18 kJ gN^{-1}) [30]. Cerrillo et al. [30] reported that membrane-based BESs can lead to high TAN RR (up to $119 \text{ gN m}^{-2} \text{ d}^{-1}$) with energy consumption in the range of $4.5\text{--}10 \text{ kJ gN}^{-1}$. Overall, bioelectrochemical TAN recovery is certainly more competitive than the Haber–Bosch process. In MECs, the increased energy demand resulting from the applied electrical energy can be partially or fully compensated by the production of energy carriers at the cathode (i.e. hydrogen [24] or methane [77]) and the microbial oxidation of waste organic compounds at the anode. Wu et al. [73] reported that the energy content of the hydrogen generated during TAN recovery in MECs was up to 142% of the electrical energy consumed. Kuntke et al. [24] reported high average volumetric hydrogen production rate of $30\text{--}50 \text{ m}^3 \text{ H}_2 \text{ m}^{-3} \text{ d}^{-1}$, while the system still required an average energy input between $7.2\text{--}9 \text{ MJ m}^{-3} \text{ H}_2$.

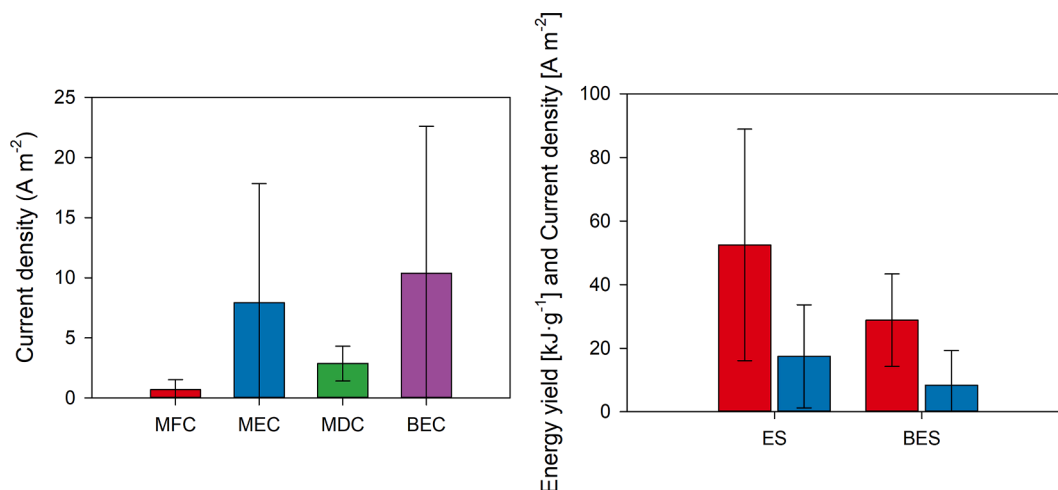


Fig. 3. (A) Current densities for different bioelectrochemical systems reported in Table 1, 2 and 3 and (B) Average energy yield (red) and current density (blue) between electrochemical and bioelectrochemical systems [31]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

6.2. BESs are limited by current density; how can we improve the current density produced?

Research aims at BESs not limited by current density. The load ratio (L_N) is a parameter that describes the ratio between current density and influent TAN concentration. Rodriguez-Arredondo et al. [28] demonstrated that current density and TAN loading rate cannot be controlled independently. The magnitude of the current density depends on COD oxidation, which in turn is influenced by several factors such as anode potential and pH. The L_N for MFC tends to be less than one, whereas for MEC it is greater than one. A L_N less than 1 means that the current density is not high enough to transfer all the NH_4^+ from the anolyte to the catholyte. Thus, in such systems, TAN load must be decreased to achieve high TAN RE. Even for values close to 1, cations other than NH_4^+ must be transported. Moreover, as operation at higher L_N s did not significantly improve TAN RE, 1.3 has been suggested to be an optimal L_N [28,43].

The most important parameters for current generation are electrode materials, biofilm development, and the nature of the organic source. The organic loading rate is essential, since exoelectrogenesis should not be the limiting step for obtaining high current density. Thus, the preferred real scenarios for ammonia recovery are highly organic concentrated streams such as pig slurry, urine or digestate. Since this is an emerging technology studied at lab-scale, most of the reviewed works use synthetic wastewaters mimicking these effluents, which contain a wide range of organic substrates with different chemical composition and biodegradability. The nature of the organic matter affects microbial activity: readily biodegradable substrates are desired when aiming for high intensities. Complex organic compounds present in real waste streams could hinder bioelectrochemical performance [102].

Therefore, urine is a paradigmatic substrate for BES (high amount of biodegradable COD) and for TAN recovery (high ammonium concentration) and has received much attention [24,32,34,54,103]. However, some compounds like urea or uric acid could not be directly used as carbon source by exoelectrogens and a previous hydrolysis/fermentation step is required [104]. Yang et al. [56] compared reject water and digestate (around 2 gN L^{-1}) and obtained much higher performance with digestate reaching TAN RE of about 40% and TAN RR rates 2.5 times higher than that with reject water.

Regarding electrode materials, BESs for TAN recovery must follow the same trends as conventional BESs. Novel anodes should have low overpotentials, as well as high conductivity, surface area, biocompatibility, and cost-effectiveness. Novel cathodes (in BEC or MEC) should aim at decreasing the overpotentials of hydrogen evolution at the cathode, while using cheaper and more sustainable materials than Pt. If TAN recovery is the main objective of the MEC, hydrogen production at the cathode may not be essential and more efficient alternatives (i.e. the use of biocathodes) can be found. Biocathodes may reduce the cathode overpotential and thus the energy requirements. For instance, Cerrillo et al. [77] coupled an electromethanogenic MEC to TAN recovery when they reduced organic matter content and upgrading biogas from digested pig slurry. The catholyte was pumped into a recovery cell with a hydrophobic membrane for TAN recovery and this led to a lower cathodic pH (7.6 with the TAN recovery system and 8.88 without) and boosted methane production ($73 \text{ L m}^{-3} \text{ d}^{-1}$) [77].

Kuntke et al. [98] and Georg et al. [95] have proposed a novel efficient way for using the hydrogen produced in the cathode as an electron donor to decrease the anode potential. They named this configuration as hydrogen recycling electrochemical system: the effluent from the MEC was fed to the anode of a parallel MEC that shared a cathode with the MEC for electrochemical TAN recovery. The recovery efficiency obtained after the MEC was 94%, while the additional treatment with the electrochemical hydrogen recycling system increased it to 99.8% [95]. No hydrogen is recovered, but energy requirements and the potential risk of chlorine evolution are reduced.

6.3. The importance of ammonium concentration in the feed

TAN recovery is designed for wastewaters with high NH_4^+ concentration since high anolyte concentrations boost NH_4^+ transport through the CEM [51–56]. NH_4^+ is expected to be the main charge carrier because of a higher concentration gradient than other cations, however, multivalent ions, even at low concentrations, are able to migrate. Lee et al. [42] demonstrated that electromigration is proportional to the initial concentration of each ion using real livestock wastewater. Nevertheless, high TAN concentrations can also hinder the biological process due to the potential inhibitory effect of free ammonia [105], which can decrease the performance and increase the start-up time in MFCs [106].

The formation of a mature biofilm on the working electrode able to tolerate high free ammonia concentration is crucial. Thus, the microbial distribution in these systems may differ from the commonly reported non- NH_3 -acclimated anodic biofilms. So far, the best method for enriching an ammonium tolerant exoelectrogenic microbial community is unknown, but a common practice is to switch from an ammonium exposed MFC to MEC rather than starting directly in MEC mode [62]. Wang et al. [107] studied the effects of free ammonia on electrochemically active biofilms in MECs and the authors reported that the threshold of electrochemical activity of anode biofilm was 1 gN L^{-1} , whereas concentrations up to 4 gN L^{-1} have been reported in acclimated biofilms (Tables 1–3). Inhibition by free ammonia in biofilms has been extensively studied [108–110]. Inhibition by free ammonia could be mitigated by lowering the pH to maintain most TAN as NH_4^+ [109,111].

High TAN concentrations may also cause undesired/uncontrolled precipitation of ammonium salts, so partial removal/precipitation of the other anions can be necessary as a pretreatment step to avoid scaling inside the BES. Alternatively, controlled precipitation of these minerals can be seen as a chemical TAN recovery method. Simultaneous N and P recovery as struvite has been described in BESs in Cerrillo et al. [30]. The major drawback with bioelectrochemical struvite precipitation has been the scaling of the cathode: the high pH close to the cathode electrode leads to the formation of struvite precipitates on the electrode, which can block mass transfer close to the cathode and thus hinder the electrochemical performance [112,113]. Simultaneous recovery of N and P by polyphosphate-accumulating organisms on the anodic side of electricity-driven BES for TAN recovery has also been demonstrated [114]. In any case, full TAN recovery via struvite precipitation is often unfeasible with TAN-rich wastewaters due to the lack of sufficient amounts of P and Mg and external dosage of these elements would significantly increase the cost of TAN recovery.

6.4. Scaling-up BES for ammonia recovery

The most studied methodologies for TAN extraction from the cathode chamber include precipitation, stripping + absorption and membrane based NH_3 extraction. These methods have already been tested at full scale without integrating them into a BES. When aiming at scaling-up, stripping + absorption is simpler than the other methods, but a high amount of energy is required for aeration. For instance, Boehler et al. [70] showed the performance of an ammonia stripping plant treating $5\text{--}7 \text{ m}^3/\text{h}$ sludge water at the Kloten-Opfikon WWTP. A CO_2 -stripper was integrated to reduce NaOH requirements.

When stripping is conducted with external air addition, oxygen intrusion can affect the bioanode performance. In MECs, NH_3 can be stripped with the gas produced (i.e., H_2), but efficient stripping requires high gas formation rates. In both cases, a separate absorption process is required after the stripping. For recovering TAN directly from the liquid, gas permeable membranes can be used. As observed, hydrophobic membranes are nowadays more widely adopted industrially than pilot scale GDEs.

Membrane-based electrodes are more complex (fouling, pressure-build up, selective NH_3 separation). However, higher efficiency and lower energy requirements are expected. Boehler et al. [70] also report

Table 3
Summary of the experimental reports on bioelectrochemical TAN recovery using MDCs and BECs.

Configuration/ Chambers	Influent Type	Electrode materials		Cathode	Recovery Methodology	Product	Current density [A m ⁻²]	TAN RE [%]	TAN RR [gN m ⁻² d ⁻¹]	Energy consumption [kJ gN ⁻¹]	Reference
		TAN [g L ⁻¹]	Anode								
Submersible MDC	Synthetic	1	Carbon paper	Carbon cloth	Stripping + Absorption	Ammonium sulfate	4.3	40.8	86.0	31.52	[85]
Triple chamber MDC	Concentrated leachate	4	Carbon brush	Carbon cloth	Stripping + Absorption	Ammonium sulfate	2.9 45 A m ⁻²	87.9 64.3	80.0 0.41	34.29 n.r.	[89]
Tubular MDC	Synthetic	7	Carbon brush	Carbon cloth coated with Pt	Stripping	Ammonium bicarbonate	80 A m ⁻²	70.0	n.r.	n.r.	[90]
Triple chamber MDC	Synthetic	1	Carbon brush	Carbon cloth	Concentration	Concentrate	1.4	75.8	11.5	n.r.	[84]
Double chamber BEC	Synthetic urine	0.70	Carbon brush	Carbon cloth	Concentration	Ammonium sulfate	2 mA	90.1	n.r.	6.48	[91]
Four chamber BEC	Synthetic	0.07	Carbon fiber brush	Stainless steel mesh	Concentration	Concentrate	2.3 ^a	n.r.	5.1	60.48	[83]
Triple chamber BEC	Synthetic urine	5.88	Graphite granules	Graphite granules	Concentration	Ammonium bicarbonate	29.3	49.5	430.0	34.23	[27]
Triple chamber BEC	Real domestic	0.06	Synthetic graphite granules	Synthetic graphite granules	Concentration	Concentrate	2.0	12.0	1.4	339.8	[26]
Triple chamber MDC	Synthetic	0.10	Graphite fiber brush	Carbon	Concentration	Concentrate	2.8 mA	42.0	n.r.	n.r.	[92]
Triple chamber BEC	Synthetic	1.02	Graphite granules/graphite rods	Stainless steel mesh	Concentration	Concentrate	3.0	75.5	23.0	21.96	[93]
Triple chamber BEC	Digested pig slurry	1.80	Carbon felt	Stainless steel mesh	Concentrate	Concentration	0.26	n.r.	0.04 gNH ₄ ⁺ d ⁻¹	n.r.	[94]
Four Chamber BEC	Soil washing wastewater	0.06	Graphite brush	Stainless steel mesh	Volatilization	Ammonia	9.8 ^a	82.5	n.r.	n.r.	[86]
Six chambers BEC	Synthetic urine	0.12	Graphite felt	Ruthenium-iridium coated Ti mesh	TMCS	Ammonium sulfate	26.0	n.r.	n.r.	12.0	[95]

^a calculated, ^b maximum value obtained, n.r. = not reported.

the performance of hydrophobic hollow fiber membranes at the Neugut WWTP to recover free ammonia gas at pH greater than 9.3 into concentrated sulfuric acid, forming ammonium sulfate. Molinuevo-Salces et al. [115] reported the results of a pilot-scale demonstration plant on a farm using gas-permeable membranes to recover nitrogen from raw manure. They reported TAN RRs of 38.20 g NH₃-N m⁻² d⁻¹ [115]. Other examples of pilot or full-scale applications of membrane-based NH₃ recovery can be found in the literature [116–118]. The use of membrane electrodes for gas extraction is complicated, for example, by membrane permeability, material conductivity, and membrane cost and scalability [46]. Membrane permeability is critical because, for a desired recovery target, it directly determines the amount of materials needed and the cost associated with the process. The conductivity of membrane cathode is also critical, as low conductivity leads to large potential drops (due to resistive losses) across the surface, demanding higher energy and leading to undesired electrochemical reactions [72]. The development of conductive polymeric membranes, including those containing carbon nanotubes (CNTs), graphene, or carbon black, has improved the performance, but conductivity is still considered low [30,72].

Despite the high TAN recovery rates obtained in lab-scale electrochemical systems, only a few studies have focused on TAN recovery in pilot scale. Ward et al. [119] recovered TAN from wastewater using a 30-cell pair electrodialysis system under applied current intensity of 20 A m⁻² with a total membrane area of 7.2 m² treating a pre-treated centrate of 75 L h⁻¹. The TAN RR was 100 gN m⁻² d⁻¹ with energy consumption of 17.6 kJ gN⁻¹. Ferrari et al. [120] coupled a 65 cell-pair pilot scale bipolar electrodialysis unit (total membrane area 3.15 m²) to a system of two liquid/liquid membrane contactor modules. This pilot plant treated 150 L h⁻¹ of anaerobic digestate with a TAN RR of 193.3 gN m⁻² d⁻¹ consuming 129 kJ gN⁻¹ under continuously applied current of 75 A m⁻² and with TAN RR of 74.9 gN m⁻² d⁻¹ consuming 22.7 kJ gN⁻¹ under intermittent current (Donnan mode). Recently, Rodrigues et al. [30] used the same 65 cell-pair pilot scale unit for pH-controlled bipolar electrodialysis treating diluted urine 41.7 L h⁻¹ and obtained TAN RR of 223 gN m⁻² d⁻¹ under current density of 100 A m⁻² with an energy consumption of 46.8 kJ gN⁻¹.

Pilot-scale TAN recovery using BES has been even less studied. Zamora et al. [74] reported for the first time the application of a scaled up MEC for nutrient and energy recovery from urine. In the first step, the system recovered phosphorus as a struvite reactor. In the second step, a MEC was coupled with a permeable hydrophobic membrane in which TAN was recovered as ammonium sulfate solution. The system was stable during the six-month operation when fed with diluted (2 times) and undiluted urine at an applied voltage of 0.5 V with an average current density of 1.7 ± 0.2 A m⁻². During stable current production, the TAN transport efficiency over the CEM was 92 ± 25% and the energy consumption for TAN recovery was 4.9 kJ gN⁻¹, which is lower than competing electrochemical nitrogen removal/recovery technologies.

7. Conclusions

Due to increasing demand, finding alternative sources for NH₃ is critical. TAN recovery from wastewater using BESs offers an interesting low-energy alternative to conventional systems. Nowadays, electrochemical TAN recovery is more applied than BESs at higher scale due to the high TAN RR reported. However, the fact that BESs shows lower energy requirements per gram of nitrogen recovered has centered the focus in BES TAN recovery. This work has compared the performance of all the reported experimental works on TAN recovery so far and has discussed on the essential factors/bottlenecks that are currently hindering its industrial adoption. TAN RR highly depends on the current density produced and the highest TAN RRs have been obtained in BECs. The nature and concentration of the organic matter is essential, as the COD has to be sufficient to generate enough current to drive the transport of ammonium. Readily biodegradable COD is preferred to prevent

fermentation/hydrolysis from being the limiting step. Ammonia concentration is a crucial parameter, as high ammonia concentration is needed to promote its transport across the CEM but too high concentrations can lead to toxicity for the biofilm. Therefore, acclimation of the biofilm to high ammonia concentration could assist in minimizing the effects of ammonia inhibition. Highly organic concentrated streams such as pig slurry, urine or digestate seem to be the best option for a fast-industrial adoption of BES-driven TAN recovery.

Among the different options for NH_3 recovery (stripping, precipitation and absorption), membranes are critical: CEM is required to transport NH_4^+ from the anode to the cathode, hydrophobic membranes may play a very important role in NH_3 transfer to the recovery chamber and AEM may be present in MDCs and BECs. Currently, stripping is the most common method used for TAN recovery in BES, as it is technically straightforward, but a significant amount of energy is required for the aeration.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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